

LEATHER TRADES CHEMISTRY

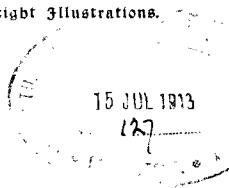
A Practical Manual on
THE ANALYSIS OF MATERIALS AND
FINISHED PRODUCTS.

BY

S. R. TROTMAN, M.A., F.I.C.,

PUBLIC ANALYST AND AGRICULTURAL ANALYST FOR THE CITY OF NOTTINGHAM.
MEMBER OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADE CHEMISTS.

With four Plates and Forty-eight Illustrations.



LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED,
EXETER STREET, STRAND.

1908.

[All Rights Reserved.]

WORKS SUITABLE FOR ANALYSTS.

In Half-Morocco. Two Volumes. Sold separately.

PHYSICO-CHEMICAL TABLES*

FOR THE USE OF ANALYSTS, PHYSICISTS, CHEMICAL MANUFACTURERS, AND SCIENTIFIC CHEMISTS.

Volume I.—Chemical Engineering, Physical Chemistry. 24s. net.

Volume II.—Chemical Physics, Pure and Analytical Chemistry.

[*Shortly.*]

By JOHN CASTELL-EVANS, F.I.C., F.C.S.

LECTURER ON INORGANIC CHEMISTRY AND METALLURGY AT THE FINSDURY TECHNICAL COLLEGE.

The Tables may almost claim to be exhaustive, and embody and collate all the most recent data established by experimentalists at home and abroad. The volumes will be found invaluable to all engaged in research and experimental investigation in Chemistry and Physics.

The work comprehends as far as possible ALL RULES AND TABLES required by the Analyst, Brewer, Distiller, Acid and Alkali Manufacturer, etc., etc.; and also the principal data in THERMOCHEMISTRY, ELECTROCHEMISTRY, and the various branches of CHEMICAL PHYSICS. Every possible care has been taken to ensure perfect accuracy, and to include the results of the most recent investigations.

THE CHEMISTRY OF MANUFACTURING PROCESSES. By BERTRAM BLOUNT, F.I.C., and A. G. BLOXAM, F.I.C. SECOND EDITION. Revised. 16s.

OILS, FATS, BUTTERS, AND WAXES. Their Preparation and Properties and the Manufacture therefrom of Candles, Soaps, and other Products. By C. R. ALDER WRIGHT, D.Sc., and C. A. MITCHELL, B.A., F.I.C. SECOND EDITION. 25s. net.

FOODS: Their Composition and Analysis. By A. WYNTER BLYTH, M.R.C.S., and M. W. BLYTH, B.A., B.Sc. FIFTH EDITION. Revised and Enlarged. 21s.

POISONS: Their Effect and Detection. By A. WYNTER BLYTH, M.R.C.S., and M. W. BLYTH, B.A., B.Sc. FOURTH EDITION. Revised. 21s. net.

DAIRY CHEMISTRY. By H. DROOP RICHMOND, F.I.C., Chemist to the Aylesbury Dairy Co. SECOND EDITION. Rewritten.

MILK: Its Production and Uses. By EDWARD F. WELLOUGHBY, M.D., D.P.H. Fully Illustrated. 6s. net.

DAIRY ANALYSIS: The Laboratory Book of. By H. DROOP RICHMOND, F.I.C. In Crown 8vo. Fully Illustrated. 2s. 6d. net.

FLESH FOODS. With Methods for their Chemical, Microscopical, and Bacteriological Examination. By C. A. MITCHELL, B.A., F.I.C. 10s. 6d.

TOXINES AND ANTI-TOXINES. By CARL OPPENHEIMER, Ph.D. Translated by C. A. MITCHELL, B.A., F.I.C. Cloth. 7s. 6d. net.

FERMENTS AND THEIR ACTIONS. By CARL OPPENHEIMER, Ph.D. Translated by C. A. MITCHELL, B.A., F.I.C. Cloth. 7s. 6d. net.

PRINCIPLES AND PRACTICE OF BREWING. By W. J. SYKES, M.D., and A. E. LING, F.I.C., F.C.S. THIRD EDITION. 21s. net.

TRADES' WASTE: Its Treatment and Utilisation. By W. NAYLOR, F.C.S. Very fully Illustrated. 21s. net.

CHEMISTRY OF GAS MANUFACTURE. By W. J. A. BUTTERFIELD, M.A., F.I.C. Vol. I., FOURTH EDITION. 7s. 6d. net. Vol. II., THIRD EDITION. *Shortly.*

PAINTERS' COLOURS, OILS AND VARNISHES. By GEORGE H. HURST, F.C.S. FOURTH EDITION. Revised. 12s. 6d.

CHEMISTRY OF INDIA-RUBBER. By CARL OTTO WEBBER, Ph.D. SECOND EDITION. Fully Illustrated. 16s. net.

GLUE, GELATINE, AND THEIR ALLIED PRODUCTS. By THOMAS LAMBERT. In Large 8vo. Illustrated. 5s. net.

THE SYNTHETIC DYESTUFFS, and the Intermediate Products from which they are derived. By J. C. CAIN, D.Sc., and J. E. THORPE, Ph.D. 16s. net.

A DICTIONARY OF DYES, MORDANTS, AND OTHER COMPOUNDS, USED IN DYEING AND CALICO PRINTING. By J. RAWSON, F.I.C., W. M. GARDNER, F.C.S., and W. F. LAYCOCK, Ph.D. 16s. net.

LONDON: CHARLES GRIFFIN & CO., LTD., EXETER STREET, STRAND.

P R E F A C E.

SEVERAL valuable books on the Leather Industry already exist, but the lack of knowledge of analytical details of modern processes has been much felt. To supply this want, the Author has endeavoured in the following pages to set forth the results of an experience extending over many years.

The International Association of Leather Trades Chemists has so stimulated work on the methods employed in Tanyard analyses that to include all would extend the book indefinitely, and the Author has therefore limited his subject to those problems which most often arise in actual practice.

In Chapter IX., dealing with the analysis of tanning materials, the historical method has been employed, since this book is designed not only for those who are conversant with the I.A.L.T.C. methods, but also for those who wish to fit themselves to undertake work in this branch of Chemistry. To the latter, a knowledge of processes, which, although no longer official, have for many years withstood criticism, is essential for a proper appreciation of the present International method.

The Author desires to acknowledge his indebtedness to the works of Professor H. R. Procter; also to the various technical journals, especially mentioning *The Journal of the Society of Chemical Industry*, from which the beautiful micro-photographs on page 164 have been reproduced.

The Glossary of Technical Terms used in the tanning industry, which is appended to this work, should prove of value to Students preparing themselves for actual practice, as Tanners have a language of their own, and most of these terms are in constant use.

S. R. TROTMAN.

NOTTINGHAM, January 1908.

TABLE OF CONTENTS.

CHAPTER I.

ANALYSIS OF FUEL,	PAGE
	1-4

CHAPTER II.

THE ESTIMATION OF NITROGEN.

Dumas Method,	PAGE 4	Kjeldahl Method,	5-10
---------------	-----------	------------------	------

CHAPTER III.

THE PREPARATION OF STANDARD SOLUTIONS.

Acids and Alkalis,	11-12	Bichromate of Potash,	13
Silver Nitrate,	13	Permanganate of Potash,	14
Sodium Thiosulphate,	13	Indicators,	14-15
Iodine,	13		

CHAPTER IV.

WATER.

The Influence of the Purity of Water used for Extracting Tanning Materials,	16-18	Analysis of Water,	19-29
Selection of Water Supply,	18	Ultimate Analysis of Solids,	29-43
		Statement of Results,	43-44

CHAPTER V.

EFFLUENTS.

General Analysis,	46-50	Standards of Purity,	58
Determination of Arsenic,	51-53		

CHAPTER VI.

DEPILATION.

	PAGE		PAGE
Lime,	50-58	Sodium and Arsenic Sulphides,	61
Ammonia and its Salts,	58-60	Spent Lime Liquors,	63-67
Sodium Carbonate and Hydrate,	60-61		

CHAPTER VII.

DELMING.

Mineral Acids,	68-72	Sulphurous Acid,	76
Formic and Acetic Acids,	72-75	Dreuches,	77-78
Lactic Acid,	73	Bran,	68-79
Boric Acid,	74-75	Dung,	79-81
Carbolic Acid,	75		

CHAPTER VIII.

QUALITATIVE RECOGNITION OF TANNINS,	82-101
---	--------

CHAPTER IX.

ANALYSIS OF TANNING MATERIALS.

Estimation of Tannic Acid,	102-106	The American Official Process,	136-140
Lowenthal Method,	106	Methods of Paessler, Weiss, and	
Hide Powder Method,	108-128	Kopecky,	140-147
Parker and Payne's Collin		International Method of Tanning	
Method,	129-132	Analysis,	147-152
Other Methods,	132-135	Colour Measurement,	153-154

CHAPTER X.

COMMON VEGETABLE TANNINS,	155-168
-------------------------------------	---------

CHAPTER XI.

MINERAL TANNAGES.

Aluminium Compounds,	169-170	Sodium Thiosulphate,	175-176
Chromium Compounds,	170-175		

CHAPTER XII.

ANALYSIS OF SPENT LIQUORS AND TANS,	177-180
---	---------

TABLE OF CONTENTS.

ix

CHAPTER XIII.

OILS.

	PAGE		PAGE
Sampling and Analysis of,	181-195	Turkey-red Oil,	199
Cod Liver Oil,	195	Tallow,	199
Bark Oil,	197	Linseed Oil,	199
Seal Oil,	197	Waxes,	200
Whale Oil,	197	Dégras,	201-204
Fish Oil,	197	Fat Liquors,	204
Neatsfoot Oil,	198	Egg Yolk,	204-206
Olive Oil,	198	Skin Grease,	206
Castor Oil,	199	Glycerine,	207-209

CHAPTER XIV.

SOAP.

Analysis of Soap,	210-214
-----------------------------	---------

CHAPTER XV.

VARNISHES,

215-216

CHAPTER XVI.

SKINS.

Structure of,	217-219	Analysis of,	222-223
Preparation of Sections,	219-222		

CHAPTER XVII.

ANALYSIS OF LEATHER.

General Analysis,	224-227	Specific Gravity,	232-233
Mineral Analysis,	227-229	Mineral Acids,	233-235
Determination of Weighing Matter,	229-230	Sulphur,	235-236

CHAPTER XVIII.

FLESHINGS AND SCUTCH,

237

CHAPTER XIX.

GLUE.

Physical Tests,	238-244	Chemical Analysis,	244-249
---------------------------	---------	------------------------------	---------

CHAPTER XX.

BENZINE

Selection of Benzine for Degreasing,	250	Analysis of,	251-255
--	-----	------------------------	---------

CHAPTER XXI.

DYESTUFFS.

	PAGE	PAGE
Determination of the Nature of a Dyestuff,	256	Analysis and Recognition of Dyestuffs, 257-282
Classification of Dyestuffs,	256	

CHAPTER XXII.

DISINFECTANTS AND ANTISEPTICS.

Salt,	283	Formaldehyde, 283-284
Phenol,	283	

GLOSSARY OF TECHNICAL TERMS USED IN THE TANNING INDUSTRY.	285
INDEX,	287

LEATHER.

CHAPTER I.

THE ANALYSIS OF FUEL.

COAL may be easily tested for ash and calorific value by the following methods :—

Ash.—About five grms. of coal are burnt in a platinum dish in a muffle.

Moisture.—Two grms. of finely powdered coal are dried between two watch glasses for two hours at 105° C., and afterwards weighed every half-hour till constant in weight.

Volatile Matter.—Two grms. of finely powdered coal are placed in a deep platinum crucible covered with a platinum lid, and ignited with a large bunsen flame till no more inflammable gas issues from the top. After one minute further heating the residue is cooled in the desiccator and the residual coke weighed; the difference in weight represents moisture and volatile matter.

Calorific Value.—From these results the calorific power can be calculated by Goutal's formula (*Analyst*, 1899, 107), which is as follows :—

$$P = \frac{8150 C + A M}{100},$$

where P = calorific power,

C = percentage of fixed carbon (*i. e.* coke - ash),

M = percentage of volatile matter = [100 - (coke + water)],

A = a coefficient which varies with the amount of volatile matter.

For M 1-15 volatile matter A = 13,000

„ 15-30 „ A = 10,000

„ 30-35 „ A = 9,500

„ 35-40 „ A = 9,000

According to De Paepe (*loc. cit.*), the results are more reliable if the following values are substituted for A, when M¹ represents the amount of volatile matter calculated on the coal supposed to be deprived of its water and ash :—

$$M^1 = \frac{100 M}{M + C}.$$

TABLE I.

A = 14,000 for M ¹	2-12
A = 12,000	„ 12-17
A = 11,000	„ 17-24
A = 10,200	„ 24-30
A = 9,400	„ 30-35
A = 8,000	„ 35-38
A = 7,900	„ 38-40
A = 7,600	„ 40-50

Direct Determination of Calorific Value.—A simple and inexpensive form of calorimeter is Rosenbain's (fig. 1), in which the coal is burnt in

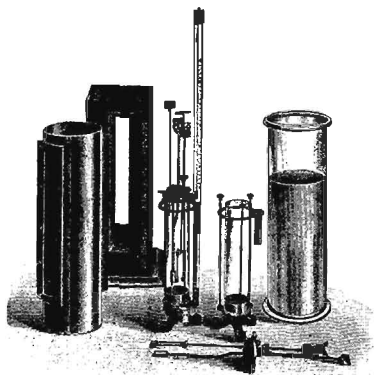


FIG. 1.—Calorimeter.

oxygen and the heat generated directly absorbed by the water of the calorimeter.

The apparatus consists of a calorimeter containing water and a combustion chamber in which the coal is burned. The calorimeter is made of polished brass, and has two glass windows, allowing the experiment to be watched. The whole is cased with wood to prevent loss of heat; the combustion chamber is removable. The coal to be tested is finely ground and pressed into the form of a small cylinder by means of a mould and screw press. The combustion chamber is made of a wide glass tube closed at top and bottom by brass plates, and if broken can be replaced by an incandescent gas-light chimney. The oxygen enters at the top, as shown in the diagram, the spent gas passing out at the bottom through a non-return valve and bubbling up through the water of the calorimeter before

escaping. The coal having been weighed and pressed into the cylinder, is placed upon the porcelain stand in the combustion chamber, the latter being then closed and placed in the calorimeter, in which a measured quantity of water has been placed. After a few minutes the temperature is carefully noted and a gentle stream of oxygen passed into the combustion chamber, the coal being ignited by an electric spark. The combustion can be watched through the window, and the stream of oxygen is regulated as required. When the combustion is complete, the valves are opened, allowing the water from the calorimeter to enter the combustion chamber, and this water is then forced out again and mixed with the rest by means of oxygen, thus bringing the entire contents of the calorimeter to one temperature. The final temperature having been carefully noted and the heat equivalent of the calorimeter itself being known, the number of units of heat evolved by the combustion of 1 gm. of the coal may easily be calculated. The following are examples of the calorific values of different coals :—

TABLE II.

<i>Class of Fuel.</i>	<i>Calories.</i>
Pure Carbon,	8080
Bituminous Coal,	8500
Good Coke,	7050
Average Welsh Coal,	8241
„ Newcastle Coal,	8220
„ Scotch „	7861
„ Derbyshire „	7733
„ Lancashire „	7717
„ Kiln-dried Peat,	5640
„ Air-dried Peat,	4250

CHAPTER II.

THE ESTIMATION OF NITROGEN.

Determination of Nitrogen.—No determination is of so much importance in tanning analysis as that of nitrogen, and it is therefore necessary to give a somewhat complete description of the process usually adopted.

There are two methods of importance, namely :

(1) Dumas Method ; (2) Kjeldahl Method.

The latter is used in tanning analysis to the exclusion of all other methods, but if an extremely accurate determination is required the method of Dumas has many advantages.

Dumas Method.—The following are the details of the method. A .

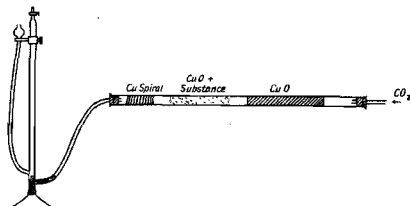


FIG. 2.—Apparatus for determination of Nitrogen.

piece of combustion tube is thoroughly cleaned by means of strong sulphuric acid, washed and dried. It is then fitted with corks and delivery tubes, one of which leads to a Kipp apparatus for the delivery of carbonic acid, the other being connected with a nitrometer, as shown in fig. 2.

The tube is then plugged with asbestos at about 6 inches from the end at which the carbonic acid enters, and about 12 centimetres of powdered copper oxide is introduced, the tube being held in nearly a vertical position. About half a gramme of the substance is then mixed

in a mortar with finely powdered copper oxide and the mixture introduced carefully into the combustion tube, the layer occupying the space of about 3 to 4 centimetres. Copper oxide is now introduced until the tube is nearly full, when a roll of freshly reduced copper gauze is inserted. The tube is then laid upon a bench and gently tapped in order to make a channel for the escape of the gases, after which it is placed in the furnace and connected with the carbonic acid generator and the nitrometer. The front portion of the tube—namely, that which does not contain the organic matter—is now heated until a dull red colour is produced. The carbonic acid is then passed through the tube until the whole of the air has been expelled. This will be indicated by the complete absorption of the bubbles as they rise in the nitrometer, which is filled with 50 per cent. solution of caustic potash. So long as any gas is collected in the nitrometer the apparatus will not be free from air. When no further increase is noticed let the gas escape by opening the tap, readjust the levels, and collect again. If, after a few minutes, no further gas is collected the apparatus will be free from air. The portion of the tube containing the organic matter is now very gently heated, the stream of carbonic acid being continued. The nitrogen which is produced will be carried through the apparatus with the excess of carbonic acid, the latter dissolving in the potash and leaving the nitrogen. The combustion is continued until there is no further increase in the volume of the gas collected—that is, until the bubbles are completely absorbed before they reach the surface. In order to complete the absorption, a little fresh potash solution is now carefully introduced by means of the cup, after which the levels are carefully adjusted and the volume of nitrogen read off. The atmospheric pressure and temperature are then taken and the volume of the gas reduced to normal temperature and pressure by means of the following formula:—

Since the volume v is measured at t° under a pressure of $B - w$, where w = tension of aqueous vapour in mm. of mercury at a temperature t° , the volume v at 0° and 760 mm. would be

$$v \times \frac{B - w}{760} \times \frac{273}{273 + t}.$$

Example.—0.2248 grm. substance gave 7.1 c.c. Nitrogen at 16° $B = 753.5$ mm., $w = 18.5$. The weight of the gas, therefore, is $7.1 \times \frac{740}{760} \times \frac{273}{289} \times 0.001251 = 0.00818$ grm., and the percentage of nitrogen = $\frac{0.00818 \times 100}{0.2248} = 3.63$.

1 c.c. of nitrogen at normal temperature and pressure weighs 1.254 mgm., hence the weight of nitrogen in mgm. contained in the quantity of organic substance taken is found by multiplying the number of cc. of nitrogen obtained by 1.254.

Kjeldahl Method.—This process depends upon the fact that most organic compounds containing nitrogen produce an equivalent quantity of ammonium sulphate when completely oxidised with strong sulphuric acid.

The ammonium sulphate is then decomposed with sodium hydrate and the resulting ammonia distilled into excess of decinormal acid, the unused portion being determined by titration. The amount of acid neutralised is exactly equivalent to the ammonia distilled over, and from this figure the nitrogen can be calculated. As much of the substance to be analysed as will contain about 0.1 gram of nitrogen is weighed into a Jena flask and 10 c.c. of pure sulphuric acid added. The flask is then placed upon a porcelain triangle, or a piece of asbestos with a circular hole of about $1\frac{1}{2}$ in. diameter, in an inclined position and heated with a bunsen or argand burner till a perfectly colourless solution is obtained. The operation is conducted in a fume cupboard, as, at first, large quantities of sulphur dioxide are evolved. The inclination of the flask should be such that the sulphuric acid vapours are, as far as possible, condensed on the upper surface. The oxidation will generally be complete in about 2 hours. The sulphuric acid must first be tested to ensure the absence of ammonium sulphate or nitric acid. This is best done by carrying out a blank experiment with pure sugar in the manner described below. It will sometimes be necessary to make a second addition of acid to complete oxidation. If the oxidation be carried out in a 300 c.c. Jena flask, after completion, the contents of the flask are cooled and diluted to a volume of about 100 c.c. with cold water, and again cooled. Fifty cubic centimetres of a 50 per cent. sodium hydrate solution are then carefully poured down the side of the flask in such a way that the heavy soda solution does not mix with the acid, but forms a layer beneath it. A fragment of pumice stone or a little zinc dust is then added (to prevent subsequent frothing or bumping), and a rubber bung is inserted in the neck of the flask through which passes a delivery tube bent twice at two right angles (as shown in fig. 16), and carrying a trap to prevent any soda being carried over and a bulb to minimise the risk of the liquid in the receiver being sucked back. The delivery tube passes on into a flask containing 50 c.c. of decinormal sulphuric acid, the end dipping beneath the surface. The contents of the Kjeldahl flask are now gently mixed and the flask heated with a naked flame till it boils. The whole of the ammonia is expelled in about 10 minutes, after which the delivery tube is rinsed with distilled water, the washings being collected in the receiver and the whole cooled. A few drops of methyl orange are then added and the excess of unused acid titrated with decinormal sodium hydrate. Each cubic centimetre of $\frac{N}{10}$ acid used is equivalent to 0.0014 gram of nitrogen. Since both the sulphuric acid and the soda are liable to contain ammonia, these must always be tested and any ammonia found deducted from the final result. This allowance is determined by treating a small quantity of pure cane sugar exactly as described above. Since cane sugar is quite free from nitrogen, any ammonia found must be due to the materials used. Of course, in a laboratory where many determinations are made, a large

quantity of soda will be made up at once. Either stick or soda powder may be used. The solution after standing till clear is decanted or filtered through a plug of glass wool into a stock bottle.

The Use of Assistants.—Organic bodies vary very much in the readiness with which they are oxidised by sulphuric acid, and hence certain assistants are often employed. The simplest of these is potassium sulphate. If 5 grms. of this compound be added to the sulphuric acid the temperature of the reaction will be considerably raised and the time necessary for oxidation correspondingly shortened. A still higher temperature may be obtained by means of sodium pyrophosphate.

A second class contains indirect oxidising agents, which, by alternating oxidation and reduction, act as oxygen carriers and greatly shorten the time of oxidation. The most important of these are metallic mercury, copper, and copper sulphate. If mercury be used a small globule weighing about 0.5 gm. is introduced with the sulphuric acid. The use of mercury introduces a somewhat undesirable complication, since, in its presence, mercuramines are formed, and it is necessary to decompose these before distilling off the ammonia. This may be accomplished by adding sufficient sodium or potassium sulphide (free from ammonia) to precipitate the whole of the mercury as sulphide. Twenty cubic centimetres of a 10 per cent. solution are generally required. Either metallic copper or a crystal of pure copper sulphate is quite as efficacious as mercury, and is not open to the same objections, no amines being formed, and consequently no sodium sulphide is necessary.

Direct Oxidising Agents.—Almost any peroxidised compound, free from ammonia, may be employed, such as potassium permanganate or potassium persulphate. If they be made use of, the first part of the oxidation is carried out with sulphuric acid only. After the first violent evolution of gas has passed, the liquid is cooled and a few crystals (weighing about half a grain) of the oxidising agent introduced, after which the heating is continued. It should be noted that potassium permanganate is very liable to contain the ammonium compound as an impurity, and Gordon Parker has suggested that its use may be dangerous in the case of substances containing much chloride, since the hydrochloric acid will be oxidised to chlorine, which would be likely to decompose ammonia. Nihoul (*J.S.C.I.*, 1901, p. 1249) strongly recommends the use of potassium permanganate, especially for leather; and his contentions are borne out by Gordon Parker (*J.S.C.I.*, 1902, p. 838).

The following are the details of his process:—

“From .6 to .7 gm. of the leather freed from fat and soluble matter is boiled with 10 c.c. concentrated sulphuric acid for half an hour, after which it is allowed to cool and a dozen crystals of potassium permanganate added. The flask is then heated again until its contents are colourless. The liquid is made up with water, including washings to 250 c.c.; 150 c.c. of 30 per cent. caustic soda solution is added and a known quantity

of zinc dust, after which the ammonia is distilled off for three-quarters of an hour, the rate of distillation being such that about 200 c.c. is collected in this time. The distillate is collected in one-fifth normal sulphuric acid. The use of mercury and of copper compounds is not recommended. If mercury be used to assist oxidation, it is necessary before distilling off the ammonia to add sufficient solution of potassium sulphide to precipitate all the mercury as sulphide, otherwise mercury amines may be formed and adversely influence the results. This difficulty does not arise with copper sulphate."

Although the process first described is largely used, particularly for agricultural analyses, no method can be really satisfactory in which the soda solution is not passed through a tap funnel, as the slightest elevation of temperature when adding the soda to the open flask must result in some

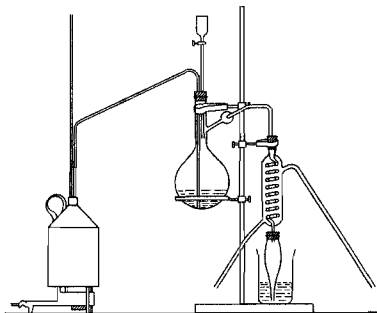


FIG. 3.

loss of ammonia. The following process, as used in the author's laboratory, is quite free from this objection:—

From .5 to 5 grms. of the substance (the quantity varying according to the nitrogen contained) is introduced into a pear-shaped Jena flask with a long neck, and 10 c.c. of strong sulphuric acid added, together with a small fragment of metallic copper foil. The flask is then placed in an oblique position and heated with a small bunsen burner until the liquid has a faint greenish tinge. In some cases a second addition of sulphuric acid is necessary, and if the substance seems refractory it is allowed to cool and 5 grms. of potassium sulphate added. The flask is inclined in order that the sulphuric acid vapours may, as far as possible, be condensed and loss by spitting avoided. When the contents of the flask are colourless or faintly green the oxidation is complete. It is then allowed

to cool, and is diluted carefully with a little water and then washed into a distilling flask of about $1\frac{1}{2}$ litres capacity. This flask is fitted with a bung through which passes a tap funnel and a delivery tube dipping beneath the surface of the liquid, through which steam can be passed. The side tube of the distilling flask is then connected with a spiral worm condenser to which is attached an adapter, as seen in fig. 3. In the flask used by the author, the side tube has been made with a trap to arrest any particles of strong alkali which violent boiling might mechanically carry over. 50 c.c. of decinormal acid are now placed in a suitable jar and placed beneath the condenser, so that the adapter just touches the surface of the acid. 50 c.c. of a 50 per cent. solution of caustic soda are then introduced by means of the tap funnel in order to neutralise the sulphuric acid. If more than 10 c.c. of sulphuric acid have been used a further quantity of soda will be necessary. Having rendered the contents of the distilling flask distinctly alkaline, a rapid current of steam is passed through until about 200 c.c. have been distilled off. The excess of unneutralised acid in the receiver is then titrated with decinormal alkali and cochineal. A blank experiment must be made with the materials. If a large quantity of soda solution is made up at once, this may be determined once and for all. The method of calculation is seen from the following example:—

Example.—0.5 gm. of glue was "kjeldahlcd," and on steam distilling into 100 c.c. of $\frac{10}{N}$ acid it was found that 48.9 c.c. of $\frac{N}{10}$ NaOH were required for neutralisation. The blank for the soda used in the steam-distilling operation was 0.7 c.c. Hence the quantity of acid used was $(100 - 48.9 - 0.7) = 50.4$ c.c. Therefore the quantity of nitrogen present is

$$50.4 \times .0014 \text{ grms.}$$

and the percentage

$$\frac{50.4 \times .0014 \times 100}{0.5} = 14.11.$$

The above method has the advantage that it overcomes the difficulty of bumping, which is very pronounced when strongly alkaline liquids are boiled, particularly in the presence of much mineral matter. Many chemists, however, prefer to boil the liquid directly, and to dispense with the condenser. The method of operation is exactly the same, except that instead of a distilling flask a round-bottomed Jena glass flask fitted with a delivery tube having a bulb blown in it as a trap to prevent sucking back is used, as shown in fig. 4. The addition of a fragment of pumice stone or a little zinc dust to the distilling flask will generally prevent bumping.

Whatever method be employed, it is very important that only Jena glass be employed for condensers and receivers, since the commoner varieties contain distinct traces of soluble alkali, which is only very slowly given up, and is quite sufficient to sensibly affect the accuracy of the results of an experiment. Phenolphthalein is inadmissible as an indicator, since it is not sensitive to ammonia. Methyl orange is satis-

factory, but the best is cochineal, which has the further advantage that the change of colour can easily be observed in artificial light.

The skin substance corresponding to the nitrogen found may be obtained from the relation: 100 parts of skin substance contain 17·8

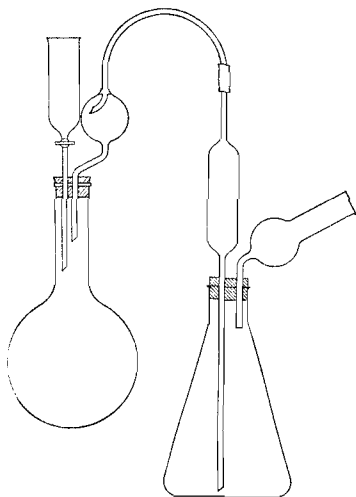


FIG. 4.

of nitrogen, or by multiplying the percentage of nitrogen by 5·62. For albuminoids and gelatine the factors are 6·25 and 5·57 respectively.

According to Gordon Parker (*loc. cit.*) there is no analytical process which can be so usefully applied to the control of the tanning process as the determination by nitrogen. By this means they can be checked at every stage and any needful modifications be made in the process.

CHAPTER III

THE PREPARATION OF STANDARD SOLUTIONS.

I. **Acids and Alkalis.**—*Normal Carbonate of Soda Solution.*—Since pure sodium carbonate is not so easy to obtain as the bicarbonate, the latter is generally employed in making up standard solutions. About 85 grms. of the salt are placed in a platinum crucible and gently heated for some time over a bunsen flame, care being taken to prevent fusion. After about ten minutes the dish and its contents are cooled in a desiccator and weighed. The dish is then reheated and weighed till constant in weight. A little more than 53 grms. of sodium carbonate will remain. This is transferred to a beaker, dissolved in distilled water, and poured through a funnel into a litre flask, the beaker being rinsed out with distilled water several times. The liquid is then cooled to 15° C., made up to the 1000 c.c. mark, and as much distilled water added as will bring the strength of the solution to exactly 53 grms. per litre. Thus if the sodium carbonate weighed 53.5 grms., the final volume will be $\frac{1000 \times 53.5}{53} = 1009.5$ c.c. The excess of water, 9.5 c.c., is carefully added from a burette. The solution is then thoroughly mixed and carefully bottled. To make a *decinormal* solution exactly 100 c.c. are pipetted into a litre flask and made up to 1000 c.c. with distilled water.

Normal Sulphuric Acid.—About 30 c.c. of pure sulphuric acid is poured into a litre flask containing about 200 c.c. of distilled water. Instead of an ordinary litre flask one graduated at 1000 c.c. and 1100 c.c. may conveniently be used. The mixture is then cooled and made up to the 1100 c.c. mark with distilled water and mixed. Ten cubic centimetres are pipetted into a beaker or small flask and titrated with the normal solution of sodium carbonate prepared above, using methylorange as indicator. The titration is repeated two or three times, the mean result being taken. The solution will, in general, be stronger than normal (i.e. 49 grms. per litre). If it is not, more sulphuric acid must be added and the solution again cooled and mixed. Now calculate what volume of water must be added to 1000 c.c. to make it exactly normal. Next remove enough of the acid with a pipette to bring the level exactly to the litre

mark and then add the necessary quantity of distilled water from a burette.

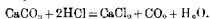
Example.—10 c.c. of the acid required 10·9 c.c. normal sodium carbonate, i.e. 10 c.c. must be diluted to 10·9 c.c. to become exactly normal.

∴ 1000 c.c. must be diluted to 1090 c.c.

Normal Hydrochloric Acid.—About 150 c.c. of strong hydrochloric acid are diluted to 1100 and treated in exactly the same way as described above.

Normal hydrochloric acid may also be standardised by means of Iceland spar, which is pure calcium carbonate.

A small piece is accurately weighed and placed in a small beaker with a measured volume of the acid. The beaker is then placed on the water bath and gently warmed till no more of the spar will dissolve, when the undissolved portion is removed, washed, dried, and weighed. From the weight dissolved the strength of the acid can be calculated from the equation



Normal Oxalic Acid.—Oxalic acid may be obtained in a state of absolute purity, having the formula $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$. It is carefully dried by exposure to air or by pressing between filter papers and the exact amount necessary for 1 litre of normal acid weighed out. Since it is, like sulphuric acid, dibasic, only half the molecular weight in grammes will be required, viz., 45 grms. or 63 grms. of the crystalline compound.

Normal Caustic Soda and Potash Solution.—The pure compound made from the metal should be used or the hydrate purified by alcohol. Ordinary sticks contain carbonates and other impurities. The former are undesirable, since their presence makes it impossible to titrate accurately with phenolphthalein, as the alkaline pink colour of this compound is immediately discharged by carbonic acid. A slight excess of the hydrate over and above that necessary for a litre of normal solution is dissolved in water and made up to 1100 c.c., titrated with normal acid and diluted as before, or its strength may be directly determined by titrating against a weighed quantity of pure oxalic acid, using phenolphthalein as indicator, adding the soda solution from a burette till a faint pink colour appears.

In a great many laboratories pure oxalic acid is the starting point for standard acid and alkaline solutions, normal caustic soda being first made by titration with this acid and the other acid solutions being standardised by means of the alkali.

In view of the importance of these standard acid and alkaline solutions—for example, in nitrogen determinations—their accuracy should be frequently checked, since careless handling of the stock bottles will often cause alterations in strength. When a solution stands in a bottle, some of the water evaporates and condenses again on the upper parts of the bottle. Hence, before using, the bottle should always be well shaken. Solutions should also always be made at a uniform temperature, since, if

the acid and alkali are diluted at widely different temperatures, they will never be exactly equivalent.

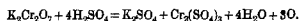
Decinormal Silver Nitrate Solution.—Exactly 17 grms. of pure silver nitrate is dissolved in 1 litre of water, or 10·8 grms. of pure silver foil is placed in a small flask, in the neck of which a funnel has been placed, and dissolved by gently warming with nitric acid. When solution is complete, the funnel is rinsed with distilled water into the flask, and the solution evaporated to dryness on the water-bath. It is then redissolved in a little water and re-evaporated to expel the last traces of acid, after which it is dissolved in water and made up to 1 litre.

Decinormal Sodium Thiosulphate Solution.—This salt may be obtained in a high state of purity, and requires only to be dried between filter papers before use. The exact quantity necessary for 1 litre by decinormal solution (24·8 grms.) may therefore be weighed out and dissolved. The solution should be made frequently, since it tends to decompose with the separation of sulphur. It should be kept in a dark cupboard.

Decinormal Iodine Solution.—Pure resublimed iodine is dried in a desiccator and weighed in a stoppered weighing bottle. After weighing, it is rapidly transferred to a beaker or flask containing a solution of 20 grms. of potassium iodide, and the bottle, etc., weighed, the exact weight of iodine taken being obtained by difference. When the iodine has dissolved it is made up to the volume corresponding to the weight taken, 12·7 grms. being required for 1 litre of decinormal solution.

Starch Solution.—This must be frequently prepared. 1 gm. of soluble starch is made into a cream with water, and poured, with stirring, into 100 c.c. of boiling distilled water.

Decinormal Bichromate of Potash.—Since a molecule of bichromate of potash contains three atoms of available oxygen which are equivalent to six monovalent atoms, one-sixtieth part of the molecular weight, i.e. 4·907 grms. per litre, is required for a decinormal solution.

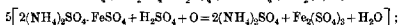
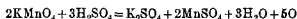


If the pure powdered and re-crystallised salt be carefully heated with stirring in a dish and cooled in a desiccator the exact amount may be weighed out, dissolved in water and diluted, but in general since potassium bichromate is not a very pure substance, the solution requires standardising. This is done by placing 10 c.c. of the solution in a stoppered bottle of about 500 c.c. capacity and adding a couple of crystals of potassium iodide, together with a little dilute hydrochloric acid. Iodine is liberated in an amount exactly equivalent to the available oxygen of the bichromate present. More potassium iodide is added if the iodine is not completely dissolved, and about 200 c.c. of water. Decinormal thio-sulphate is then run in from the burette, the stopper being replaced and the bottle shaken after each addition. When only a slight yellow colour is left, a few drops of the starch solution are added and the titration continued

until the blue colour of the starch is just discharged. The bichromate solution is then diluted till it is exactly equivalent to the thio sulphate.

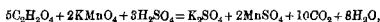
Standard Potassium Permanganate Solution.—For tannin titrations a stock solution of 5 grms. per litre is kept, which is diluted in the proportion of one in five and titrated with tannic acid before use (see Chapter IX.).

A *decinormal solution* may be prepared by dissolving 3.16 grms. in 1 litre of distilled water. Although obtainable in a pure state, the solution generally alters a little during making, probably owing to oxidation of organic matter. It therefore requires standardising. The best substance for this purpose is either ferrous ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, or crystalline oxalic acid. In either case a small quantity of the substance is weighed and dissolved in water. If the sulphate be employed some dilute sulphuric acid is added, and the permanganate is run in from a burette with stirring till a faint pink colour is produced, indicating that all the ferrous iron has been oxidised. If, during the titration, a brownish coloration is observed, more sulphuric acid is required to keep the iron and manganese sulphates in solution—



or, since ferrous ammonium sulphate contains one-seventh of its weight of iron, the exact value of the permanganate in terms of iron can easily be calculated.

If oxalic acid be used the titration is carried out in exactly the same way, except that the solution of the oxalic acid must be kept warm (about 60° C.). The reaction proceeds in accordance with the equation,



i.e. 90 parts of oxalic acid require 16 of oxygen, or 63.2 of potassium permanganate; hence the oxygen value of the permanganate solution can be calculated.

II. Indicators for Acids and Alkalis.—*Litmus Solution.*—10 grms. of litmus is digested with 500 c.c. of distilled water and filtered, and sufficient nitric acid added to produce a violet colour.

With acids it gives a bright red colour, turning blue with alkalis. It is sensitive to carbonic acid, and can only be used to titrate carbonates if the liquid is boiled after each addition of acid to expel carbonic acid.

Phenolphthalein.—1 gm. is dissolved in a litre of methylated spirit and dilute soda added till a very faint pink colour is produced. Phenolphthalein is pink in alkaline and colourless in acid solution. It cannot be used in the presence of carbonic acid.

Methyl Orange.—0.5 gm. is dissolved in a litre of water. The solution is red in acid and yellow in alkaline solutions. It is only very slightly sensitive to carbonic acid, but is not very sensitive in hot solutions, and the change of colour is difficult to see in yellow light. A Neapst

lamp is, however, satisfactory. Methyl orange is not sensitive to organic acids.

Cochineal Solution.—About 2 grms. of cochineal is dissolved in 250 c.c. 30 per cent. alcohol. It is yellowish red in acid solution and changed to violet by alkalis. It is very suitable for artificial light and solutions containing ammonia (such as Kjeldahl determinations), and is not much affected by carbonic acid. It is not suitable for organic acids.

Alizarine Solution (see p. 34).

CHAPTER IV.

WATER.

The influence of the purity of the water used for extracting a tanning material cannot be over-estimated. The presence of even small quantities of impurities may seriously affect the amount of tannin extracted. To illustrate the importance of these points the work of Nihoul may be quoted, on "The Influence of the Nature of the Water used in the Extraction of Tanning Materials" (*J.S.C.I.*, 1901, 1005; and *Collegium*, 1903, 175, 182).

Oak bark, pine bark, valonia, and sumach were extracted with five waters of varying hardness in hot and cold solutions, observing I.A.L.T.C.¹ conditions. Analysis of the extracts, and comparison with those obtained with distilled water, showed that the use of natural waters caused a loss of tannin, an increase of non-tannins, and slight weighting of the hide, owing to absorption of salts from the water.

A water containing much chloride caused a serious loss of tannin in the case of oak bark, pine bark, and sumach, but wasted little valonia. Hard waters used hot caused loss of tannin in all the materials tried, amounting, in the case of sumach, to nearly half that extracted by distilled water. The extractive powers of waters used cold, though lower, varied less for the different waters, and with very hard water cold extraction was as profitable as hot extraction, and, in the case of sumach, more so.

To gain some knowledge of the individual action, in tannin extraction of the various mineral constituents of natural waters, Nihoul prepared artificial solutions of calcium and magnesium bicarbonates and used them for extracting oak bark, pine bark, and sumach. He employed solutions of three strengths, corresponding to 10, 20, and 30 parts of hardness per 100,000.

Oak Bark.—The organic extract was practically uninfluenced by the bicarbonate, but non-tannins were notably higher and increased with the degree of hardness, whilst tannin showed a corresponding diminution, reaching a maximum of 2.11 per cent., the magnesium bicarbonate causing a more marked difference than the calcium salt.

¹ International Association of Leather Trades' Chemists

Pine Bark.—The percentage of tannin upon the organic extract was higher than with oak bark.

Sumach.—Similar results, but sumach seemed to give up more to magnesium bicarbonate than to the lime salt, the loss of tannin with the first amounting to 3.39 per cent. in the solution of greatest hardness. Also, the organic extract increased with the amount of bicarbonate in the water.

The loss in tannin may be strongly influenced by the mixture of an acid salt with a bicarbonate, when a state of chemical equilibrium would be established, by which a part of the acid would be set free and accelerate the extraction of tanning material.

Calcium and magnesium bicarbonates seem to have the power of partially decomposing the tannin into matter not absorbed by hide powder, the organic extract being little affected, whilst the amounts of tannin and non-tannin are influenced inversely.

Influence of Chlorides and Sulphates.—Chlorides have such a marked destructive effect on the tannin as to account completely for the losses observed with natural waters. A natural water containing 0.4655 gm. of chlorine per 1000, all as CaCl_2 , caused a loss of 4.80 per cent. of tannin in the case of pine bark; and an artificial water containing 0.5 gm. of chlorine per 1000 wasted 4.88 per cent. The loss was greater in the case of sumach. Water containing 0.4 to 0.5 gm. of MgCl_2 per 1000 has a marked solvent action on non-tannins, a 0.1 per cent. solution increasing the non-tannin from 4 per cent. with distilled water to 25.5 per cent. in a pine bark extract.

The influence of chlorides upon extraction is due both to the salt and to the tanning material; not only the tannin in the latter but also various constituents of the non-tannins come into play. The loss of tannin from oak bark is roughly proportional to the strength of the saline solutions. Except for calcium chloride this is true for sumach. But with pine bark regularity is only observed in the extracts with solutions of magnesium chloride. The destructive influence of the various chlorides is in some cases proportional to their molecular weights.

Influence of Sulphates.—Combined sulphuric acid has a greater destructive influence than combined chlorine, pine bark and oak bark suffering more than sumach. The relation between the loss in tannin and the strength of the salt solution is similar for each tanning material and each salt, but more than in the case of chlorides.

The results further show that the evil effects of hard water are not altogether avoided by chemical softening. Salts of sodium are not only not harmless, but in some cases, as in that of pine bark, also produce more loss than the calcium or magnesium compounds, so that a naturally soft water is of greater advantage than hitherto imagined. The mineral matter fixed by the hides indicates an important interaction between the

formed, capable of absorption by the hide substance, or tannin combines with the base of the salt and free acid is liberated. Hence, owing to the fixation of mineral matter, the ash of leather will vary in amount according to the water used in manufacture, and analysts must allow a certain latitude in the matter. The presence of sulphates in the ash of leather supposed to contain none may also be explained by the presence of sulphates in the tannery water.

Selection of Water Supply.—The selection of a water supply is thus a matter of supreme importance to tanners, an unsuitable one frequently causing serious and sometimes obscure trouble. For a tannery, water should be as free as possible from organic matter, since water so contaminated invariably contains a large number of putrefactive organisms liable to set up bacterial action and damage the skins. Next to organic matter, perhaps the most objectionable impurity is iron, since it combines with the tannin and forms stains on the skins which cannot be removed. Less actively injurious is common hardness. Carbonates of calcium and magnesium are precipitated in the tissues of the skin substance and make the leather hard; or they react with the tannin acids, forming compounds which darken by oxidation and stain it. For all operations, except liming, where impurity matters little, the purer or the softer naturally the water is, the better. The addition of precipitants and softening agents to improve the water for one purpose often leaves it still unsuitable or makes it more so for another. Thus treatment for permanent hardness with soda, while removing the calcium compound, which is itself objectionable, produces soluble sodium sulphate, shown by Nihoul¹ to be more harmful in tannin extraction than either the calcium or magnesium salts. The addition of baryta meets the difficulty better, but is expensive. Chlorides are irremovable by any practicable method, and, whether those of calcium, magnesium, or sodium, have a destructive effect on tannin sufficient to account completely for the loss of it observed in using natural waters for extraction. Nihoul's research on the influence of the salts dissolved in natural waters upon tannin extraction has, indeed, emphasised the great value of a naturally soft water in the tan-yard. In its absence an exact knowledge of the constituents of the available supply is important so that it may be rendered as efficient as possible artificially.

The analysis of water includes the determination of

- (1) Total dissolved solids.
- (2) Suspended matter.
- (3) Chlorides.
- (4) Nitrates and nitrites.
- (5) Organic matter, saline and organic ammonia.
- (6) Temporary and permanent hardness.

The information given by these figures will be sufficient for most

purposes, but it may often be necessary to extend the analysis to a determination of oxygen absorbed by the organic matter present and the quantitative estimation of the mineral constituents.

(1) **Total Dissolved Solids.**—Fifty to a hundred cubic centimetres of the filtered water are evaporated to dryness in a weighed platinum or nickel dish on a water-bath, then dried in a steam oven, cooled in a desiccator, and weighed. The quantity of water taken will, of course, vary with the expected amount of dissolved solids. In the case of very pure water as much as 250 c.c. may sometimes be necessary. In weighing the solids it is important to remember that they are usually extremely hygroscopic, and must therefore be weighed quickly. If a platinum dish be taken from a desiccator and allowed to stand in a balance case, it will be observed that for some time it increases in weight owing to the property which platinum has of condensing water vapour at its surface. To prevent error due to this, as well as to obtain results which will compare with each other, the same interval between placing in the desiccator and weighing should always be allowed to elapse.

Some information as to the nature of the water may be obtained by carefully igniting the total solids at a low red heat. In the presence of much organic matter a slight blackening in colour will generally be observed, accompanied by a considerable loss in weight. In order to correct for any carbonates that have been decomposed by over-heating, the residue should be moistened with a solution of ammonium carbonate, reduced in the oven and very gently heated. Any lime that may have been produced by the first heating will be reconverted into carbonate.

If the presence of carbonate of soda be suspected the total solids may be extracted with freshly-boiled distilled water, filtered, and the filtrate titrated with decinormal acid and methyl orange. It is very essential to boil the water, since if it contain any carbon dioxide it will dissolve the carbonates of lime and magnesia present in the total solids.

The loss on ignition should not exceed 20 per cent. of the total solids, but the information given by the test is not very reliable. If a detailed examination of the constituents of the total solids is required, from 500 to 1000 c.c. are acidified with nitric or hydrochloric acid, evaporated to dryness, and examined as described on page 39.

In a good water the dissolved matter rarely rises above 50 parts per 100,000. A higher value would in most cases indicate excessive hardness.

(2) **Suspended Matter.**—This may be estimated, if necessary, by agitating the water thoroughly and withdrawing 50 c.c. with a pipette before the sediment has settled. If this be evaporated to dryness and weighed, the excess of weight above that of the dissolved solids, determined as above, is due to suspended bodies. A more accurate method is to filter 250 c.c. of the water through a weighed dried filter paper and dry and weigh the residue. The filter paper should be first thoroughly washed with distilled

water, and when nearly dry placed in a stoppered tube and dried until it no longer loses weight. After filtering off the suspended matter the paper is redried in exactly the same way until of constant weight. The increase in weight is due to the suspended matter. The following method has some advantages:—

Two hundred and fifty c.c. of the sample are allowed to stand in a cylinder (A), provided with a draw-off tap about 40 or 50 millimetres above the bottom (fig. 5). Allow to settle for 3 hours, and then run the top clear liquid off into a similar cylinder (B). If quite clear, this may be discarded. The liquid in the first cylinder containing the suspended matter is filtered through a weighed Gooch filter, containing a mat of asbestos cream and protected by a perforated lid. If the precipitate is voluminous or shining, it should be digested with water before filtering. The Gooch filter and its contents are well washed with boiling water, dried at 110° C., and weighed.¹

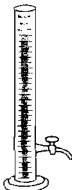


FIG. 5.

A quicker method of separating the suspended matter is to place the sample in a small centrifugal machine, driven at about 2000 rev. per minute by a small electric motor or by hand. The clear liquid is discarded and the solid matter weighed as above.

Examination of Suspended Matter.—Valuable information concerning the nature of a water may often be obtained by a microscopical examination of the suspended matter. This may be readily procured by filtering a litre of the water through a hard filter paper (Schleicher & Schüll, No. 605) in the manner illustrated by the diagram. When the water has all run through, the sediment is washed off the filter paper by means of a fine stream of water from a wash-bottle. A little of it is then spread upon the surface of a cover slip and mounted in glycerine or water. If preferred, the water may be filtered through a Pasteur candle by means of a filter pump. The filter is then stood in a small dish and the adhering sediment removed with a camel-hair brush and a little water.

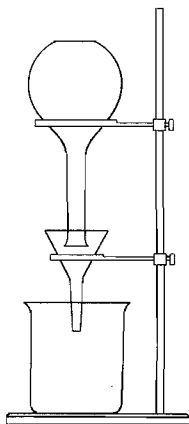


FIG. 6.

Colour.—The measure of the colour is a very useful indication of its purity. It is of special value where one has to periodically examine the same water, as when the colour constants have once been determined, any marked variation will undoubtedly point to some d

¹ "Method of Ribble Joint Committee," see *Trades Waste*, W. Naylor, p. 70.

turbing influence which should be sought for. In the author's laboratory the colour of water is measured by Lovibond's tintometer (*q.v.*) by placing the two-decimetre polarimeter tube full of the water between the instrument and the light and matching the colour with the standard glasses. The following are some of the tints obtained with polluted river water:—

TABLE III.

	Black.	Orange.	Yellow.
No. 1	0.5	0.0	0.2
No. 2	0.7	0.0	0.8
No. 3	0.1	0.2	0.6

If, instead of using a tube of constant length, a varying length be substituted, still more useful information may be obtained, since the coefficient of absorption of the different colours would be different for each of the different colouring matters, and thus a differentiation can be obtained in some cases where the colours were apparently the same when observed in a tube of fixed length.

As a general rule it will be found that a yellow or brown tint indicates sewage pollution (except in case of peat waters) or the presence of iron. Green is sometimes produced by organisms containing chlorophyll, while of course trade refuse will produce very distinct colour indications depending upon the nature of the discharge. A simple apparatus for measuring the colour of water has been described by W. T. Burgess (*Analyst*, 1902, p. 294).

The water to be observed is placed in a 2-foot tube placed side by side with a similar tube containing distilled water. Reflected light from the surface of a white card or porcelain slab passes through the tubes and impinges at the other end upon a plane mirror which is fixed at an angle of 45° so as to reflect the light vertically upwards. Above the mirror is a small platform with two circular apertures. Over each aperture stands a cylindrical glass, the whole being covered with a cardboard screen. Distilled water is placed in the cylinder through which the light from the water under examination passes, while in the other a standard colour solution is run until the two colours are exactly matched. The standard solution is made as recommended by Crookes, Odling and Tidy (*Analyst*, 1902, p. 294), by dissolving 1 grm. of cobalt sulphate and 0.05 grm. of potassium bichromate in a litre of water.

(3) Chlorides.—The determination of chlorides is of considerable importance in waters to be used for tanning, for not only do they indicate sewage pollution, but their presence prevents a water from completely extracting tanning materials, while if any quantity of magnesium chloride be present in a water to be used for a boiler, hydrochloric acid will be liberated by the superheated steam and cause considerable trouble.

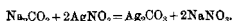
Chlorides in water are estimated by titration with a standard solution of silver nitrate, using potassium chromate as an indicator. A cent

normal solution of silver nitrate is made by diluting 100 c.c. of the decinormal solution with distilled water to a litre. Each cubic centimetre will be equivalent to .000355 grm. of chlorine or .000585 of sodium chloride. The potassium chromate solution is made by dissolving 1 grm. of the salt in a litre of water. This solution must be carefully tested to ensure that it is sensitive. For this purpose .5 c.c. are placed in a beaker with distilled water and the silver nitrate solution carefully run in from a burette with stirring. If more than one drop is required to produce a reddish coloration, the volume necessary must be carefully read off and deducted from the volume used in subsequent experiments. It must not be forgotten that distilled water occasionally contains free hydrochloric acid.

One hundred cubic centimetres of the water to be analysed are now measured into a beaker with a pipette and placed upon a white tile beneath the burette. The silver nitrate solution is carefully run in with constant stirring until a faint red tint due to the formation of silver chromate is observed. The volume of silver nitrate used is then read off and calculated into chlorine. For example :

100 c.c. of water required 10.5 c.c. of silver nitrate.
 \therefore 100 c.c. of water contained $10.5 \times .000355$ grm. of chlorine ;
i.e. " " " " " .0037275 " "
 and 100,000 parts will contain 3.73 of chlorine.

Natural water is occasionally met with which contains free carbonate of soda. In such a case the chlorides will be too high, since silver nitrate is decomposed by alkaline carbonates with the formation of silver carbonate in the same way as chlorides.



When alkaline carbonates are suspected the total solids must be extracted with hot distilled water and filtered, washing the residue several times. The filtrate is then titrated with decinormal acid, and the volume of $\frac{N}{10}$ acid required multiplied by 10 is the equivalent of the alkaline carbonate in $\frac{N}{100}$ silver nitrate. This volume deducted from the total volume of centinormal silver nitrate required by the original water gives as difference the true equivalent of the chlorides present.

E.g. 100 c.c. of water wanted 40 c.c. of $\frac{N}{100}$ AgNO_3 solution.

Filtrate from total solids wanted 1.5 c.c. $\frac{N}{10}$ acid = 15 c.c. $\frac{N}{100}$ "

\therefore the chlorides in 100 c.c of water = $(40 - 15) = 25$ c.c. "

The value of chlorides as a factor in forming an opinion upon a water supply is very great. As a general rule it may be said that any water

containing more than two parts of chlorine per 100,000 must be regarded with suspicion, unless its presence can be satisfactorily explained.

For tanning purposes excess of chlorides must be avoided, since, as already stated, their presence considerably interferes with the extraction of tanning materials.

While the absence of chlorides is clearly indicative of freedom from sewage pollution, the finding of a quantity is not sufficient to condemn a water unless accompanied by the signs of recent contamination. Chlorides occur extensively in many geological strata, and the writer has occasionally found abnormal amounts where no confirmatory evidence of present pollution could be obtained, even by bacteriological analysis.

(4) **Nitrates and Nitrites.**—All waters contain nitrates which are produced by the oxidation of nitrogenous organic matter. Occasionally nitrites are also met with either as deoxidation products of nitrates or an intermediate stage in the oxidation of organic matter. While the presence of nitrates does not necessarily imply the actual presence of sewage matter, it raises a ground for suspicion, since nitrates in any quantity invariably point to past sewage pollution.

Nitrates may be determined in a great many ways, of which only a few will be described.

(a) *Nitrometer Method.*—This is undoubtedly the best and most accurate way of determining nitrates, but requires a rather long time when only traces are present. It is carried out as follows:—From 100 to 250 c.c. of water are evaporated on a water-bath, the residue extracted with water and filtered to remove calcium and magnesium carbonates. The filtrate is evaporated in a small beaker or dish until it measures about 5 c.c., and transferred to the cup of a nitrometer filled with mercury, rinsing out the beaker with a few drops of water. By carefully turning the three-way tap the liquid is drawn into the limb of the nitrometer, and in the same way about 10 c.c. of concentrated sulphuric acid are introduced. After a few minutes any air which may have got in is carefully expelled by opening the tap and raising the free limb of the nitrometer. Having seen that the tap is secure, the graduated tube of the nitrometer is taken in the right hand, and, resting it on the left, is depressed to an angle of 45° to 60°, at the same time bringing the liquid into contact with the mercury by a rotary movement of the right hand. It is important that the upper portion of the column of mercury should be completely broken up, or reduction will not readily take place. After agitating for about five minutes the tube is replaced in the stand, the level of the mercury adjusted, and the volume of the gas read off. The shaking is repeated until no further increase of volume takes place. At this point all the nitric acid has been converted into its equivalent of nitric oxide. A sufficient time is now allowed to elapse for the liberated gas to reach the temperature of the air, which, together with the barometric pressure, is carefully noted and the gas then brought to atmospheric pressure by

adjusting the level of the mercury in the open tube until on opening the tap there is no tendency for the gas to escape or air to pass in. The volume of the gas is now read and the weight of nitrogen which it contains calculated. Instead of calculating the nitrogen the result may be rapidly obtained by introducing 5 cubic centimetres of a standard solution of potassium nitrate into a second nitrometer and observing the volume of nitric oxide produced. The advantage of this method is that no corrections are necessary.

The method of calculation will be clear from the following example:—

Five hundred c.c. of water yielded 3.3 c.c. of nitric oxide. The atmospheric pressure was 766 mm. and the temperature 20° C. Therefore the volume of the nitric oxide under normal conditions of temperature and pressure is $\frac{3.3 \times 273 \times 766}{293 \times 766} = 3.3 \times 0.939$, the weight of nitrogen contained

in this volume of nitric oxide is $3.3 \times 0.939 \times 0.0000896 \times 7 = 0.00195$.

∴ 100,000 parts of water contain 0.39 part of nitrogen as nitrate.

(b) *Estimation by Reduction to Ammonia*.—Some fragments of zinc are immersed in a dilute solution of cupric sulphate till they are just covered with metallic copper. The zinc copper couple thus obtained is washed and about 5 grms. used for each reduction. It is necessary to prepare it freshly for each experiment. One hundred c.c. of the water are placed in a stoppered bottle with the zinc copper couple and about a gramme of pure oxalic acid added to precipitate lime.

After about twelve hours an aliquot portion of the clear liquid is withdrawn and made up to 50 c.c., the ammonia it contains determined by means of Nessler solution and calculated to nitrate. It is obvious that this method is not admissible in the case of water containing much ammonia, unless it be boiled for some time and then made up to its original volume.

(c) *Indigo-Carmine Method*.—Five grms. of indigo-carmine are made into a paste with water and dissolved in a litre of dilute sulphuric acid (free from nitric acid) and filtered. A standard solution of potassium nitrate containing .722 gm. per litre is also prepared. The indigo-carmine solution is now standardised by placing 5 c.c. of the nitrate solution in a small beaker or dish provided with a stirrer, warming and carefully running in the indigo-carmine until the blue colour is just permanent. Since each cubic centimetre of the nitrate solution contains .001 gm. of nitrogen the value of the indigo-carmine solution can easily be calculated. Two hundred and fifty cubic centimetres of the water under examination are concentrated and titrated in an exactly similar way and the results calculated into nitrogen per 100,000 parts.

This estimation may be more accurately carried out on the same principles as a Löwenthal estimation of tannin, the solutions required in both cases being identical (Trotman and Peters, *J.S.C.I.*, 1902, 694).

From 5 to 20 c.c. of the water under examination are mixed with

25 c.c. of indigo-carmin solution. To this is added dilute sulphuric acid equal in amount to the united volumes of the water and indigo-carmin solution. The whole is then heated on the sand-bath for 15 minutes. At the end of this time the excess of carmin solution is titrated with a standard solution of potassium permanganate. In a similar manner, simultaneously with the above, a blank estimation is done, replacing the water under observation by distilled water. The difference between the two titrations is the amount used by the nitrates in the water.

The permanganate solution is standardised by means of standard solution of potassium nitrate containing 0.0001 gram. of N per c.c.

(d) *Phenol Sulphonate Colorimetric Method.*—Benzene disulphonic acid, $C_6H_4OH(SO_3H)_2$, is prepared by mixing 18.5 c.c. of strong sulphuric acid and 1.5 c.c. of water with 3 grams. of phenol. Fifty c.c. of the water are evaporated on the water-bath in a platinum or porcelain dish, and to the residue is added 1 cubic centimetre of the sulphonate. After well mixing with a glass rod, the dish is placed on the water-bath for some minutes, a few drops of water are added, as also about 2 c.c. of sulphuric acid, and the mixture warmed again on the water-bath until a faint yellow colour is produced by the formation of picric acid, $C_6H_2OH(NO_2)_3$. The liquid is now diluted with a little water, washed into a Nessler cylinder and excess of ammonia added, when a marked yellow tint will be produced owing to the formation of ammonium picrate. The liquid is made up to 100 c.c. and matched with a standard solution of potassium nitrate (722 gram. per litre) as follows:—Five cubic centimetres (0.05 gram. N) are treated as above, the two cylinders placed upon a white tile and their tints compared by looking vertically down upon them. If the colour of the standard is darker than that of the sample, pour some out into a similar graduated cylinder until the two tints are nearly the same, making up the diminished volume to 100 c.c. again for a final comparison. The tints being matched, the nitrate in the sample is equal to that in the volume of standard solution originally taken, less the portion poured out.

If the standard be the lighter, then similarly some of the sample is poured away until the tints are equal, when the volume left contains the same quantity of nitrogen as the standard, i.e. 0.05, and the quantity contained in the original 100 c.c. can be easily calculated. An advantage of this method is that it can be applied to the total solids obtained in the course of analysis. It is, however, apt to give low results in the presence of much chloride.

Nitrites may be tested for qualitatively by placing 100 c.c. in a Nessler cylinder with a few drops of dilute sulphuric acid and adding 1 c.c. of a 5 per cent. solution of metaphenylene diamine in dilute sulphuric acid. In the presence of nitrites a yellow colour is developed, and by matching the colour with a standard solution of potassium nitrite, the quantity present may be approximately estimated. A second test depends

upon the fact that nitrous acid is able to liberate iodine from potassium iodide. The water under examination is acidified with dilute sulphuric acid in a stoppered bottle, and a few drops of potassium iodide solution added with agitation. If now a little chloroform be introduced into the bottle and the whole well shaken for some minutes, in the presence of nitrites the chloroform will be distinctly coloured pink by the liberated iodine.

(5) **Determination of Organic Matter.**—An idea of the amount of organic matter present in a water may be obtained by a determination of its free and albuminoid ammonia by Wanklyn's process and the oxygen it is able to absorb.

Wanklyn's process depends upon the fact that nitrogenous organic matter when boiled with a solution of alkaline permanganate gives up a definite portion of its nitrogen as ammonia. The method is somewhat empirical, but is universally used in preference to the ultimate analysis of the water residue, as in Frankland's combustion process. In this the water is evaporated with sulphurous acid solution to get rid of carbonates, nitrates, and nitrites. The removal of the last traces of nitrates is effected by the addition of ferric chloride, and is often difficult when they are present in any quantity. It is also very necessary to exclude organic matter and dust during the evaporation. The residue is ultimately burnt, as in an ordinary combustion, the gases being received in a eudiometer and measured. A good water when examined in this way should not yield more than 0.2 part of carbon or 0.02 of nitrogen per 100,000 parts. While in some respects the process is superior to the albuminoid ammonia determination, it has nevertheless become practically obsolete, chiefly because it gives no information upon the condition of the carbon and nitrogen, and in a water it is the state of combination of these elements rather than their quantity which is of importance.

For Wanklyn's process the following solutions are required:—

1. Standard solution of *ammonium chloride* made by dissolving 3.15 grms. of the pure salt in a litre of water. Each cubic centimetre of this solution will contain .0001 gm. of ammonia. It is diluted as required for use to one-tenth of this strength, *i.e.* to .00001 gm. per c.c.

2. *Nessler Solution.*—This is a solution of the double iodide of mercury and potassium, HgI_2KI , in caustic potash which, in presence of ammonia, gives rise to a brown colour, the depth of which is proportional to the quantity of ammonia present, and hence may be used as a means of determination.

The solution is made as follows:—

Dissolve 35 grms. of potassium iodide in about 100 c.c. of distilled water, and add to it a cold solution containing 16 grms. of mercuric chloride in about 300 c.c. distilled water, when it will be found that a slight permanent precipitate is produced. The mixture is then made up to 1000 c.c. by the addition of 20 per cent. NaOH .

This solution should be prepared some days before use, as, when freshly prepared, it is not always sensitive. Its sensitiveness should be carefully tested from time to time. It may be conveniently stored in a bottle fitted with a rubber bung through which passes a 2 c.c. pipette, as shown in fig. 7. The required quantity can in this way always be obtained without any danger of sucking the solution into the mouth or disturbing the sediment, which a layer of broken glass will also help to keep down. The sensitiveness of Nessler's solution increases with keeping, and, when used, three minutes should be allowed for the development of the full tint.

Alkaline Permanganate Solution.—Powder finely 8 grms. of potassium permanganate and add it little by little, with constant stirring, to about 200 c.c. of boiling water in a beaker, place on a sand-bath, and boil gently for a few minutes to ensure complete solution. In a separate vessel dissolve 120 grms. of sodium hydrate in water, mix the two solutions together, and make up to about 1200 c.c. to allow for subsequent concentration. Place the solution in a large retort or distilling flask connected with a condenser and distil until 50 c.c. of the distillate no longer give any colour on standing for three minutes with 2 c.c. of the Nessler solution. Then cool, and pour into a stoppered bottle.

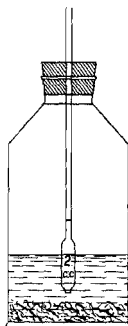


FIG. 7.

Ammonia-free Distilled Water.—The water used for dilution should, of course, be ammonia-free, and even laboratory distilled water rarely fulfils this condition unless freshly distilled. If 50 c.c. of it standing for three minutes in a covered vessel with Nessler's solution gives no coloration it may be safely used; if not, some must be distilled with a pinch of ignited sodium carbonate, rejecting the distillate so long as it affects Nessler's reagent and then storing in a carefully stoppered bottle.

Determination of Free Saline Ammonia.—Five hundred c.c. of water are placed in a distilling flask of about 1½ litres capacity, connected with a suitable form of condenser and boiled until the distillate no longer gives any coloration with Nessler's solution. Unless the apparatus is in constant use this preliminary cleansing must never be omitted. A very useful form of condenser, both efficient and economical in space, is the "Cribb," as shown in fig. 8. Having freed the apparatus from ammonia the water is poured away and 500 c.c. of the sample under examination introduced together with a pinch of ignited sodium carbonate. One hundred c.c. are distilled off, well mixed, and 50 c.c. poured into a glass cylinder of about 100 c.c. capacity, 2 c.c. of Nessler solution are then added and the colour at the end of 3 minutes observed.

Into a second Nessler cylinder a small quantity (say 5 c.c.) of the diluted standard ammonia solution is run in from a burette, made up to 50 c.c. with ammonia-free distilled water, and 2 cubic centimetres of Nessler solution added. After allowing 3 minutes for the colour to

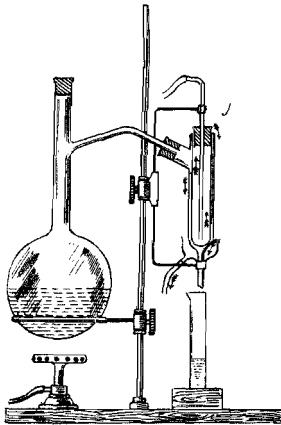


FIG. 8.

develop, the two cylinders are placed side by side upon a white porcelain tile and the colours compared by looking vertically down through the liquid. If the two tints are identical the quantities of ammonia in the two cylinders are the same, i.e. equal to $\cdot 00005$, and this multiplied by 2 gives the amount present in the original 500 c.c. of water. If the colours of the two solutions are not identical, fresh trials must be made with varying quantities of the ammonium chloride solution until the colour is matched. It will not do to add more ammonium chloride after the Nessler solution, but the experiment must be begun anew each time. While Nesslerising the first distillate a further 50 c.c.

are distilled off and tested in the same way. It will generally be quite free from ammonia, but if any be found the distillation must be continued till the distillate is free, the quantities being added to that obtained in the first experiment.

Albuminoid Ammonia.—Fifty c.c. of the alkaline permanganate solution are now added to the contents of the flask, the distillation continued and the ammonia estimated in exactly the same way as described above. It is well to thoroughly mix the permanganate by a rotary movement of the flask before commencing the distillation, or bumping will often ensue.

Much time may be saved by using Lovibond's tintometer instead of matching the colour with ammonium chloride solution.

The Nesslerised solution to be tested is placed in a half-inch cell and its colour matched with a series of glasses corresponding to definite quantities of ammonia.

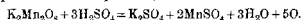
The determination of ammonia is an important one in water intended for tanning purposes, since excess of this constituent practically always indicates sewage pollution, especially if accompanied by chlorides and nitrates. Polluted water will generally contain putrefying organisms.

whose introduction is always undesirable. In general terms any water that contains more than 0.025 part of either free or albuminoid ammonia should be viewed with suspicion for tanning purposes.

Estimation of Organic Matter in Water by Kjeldahl's Method.—Half a litre of water is boiled down to a small volume, free ammonia being thus expelled, and is then transferred to a round-bottomed Jena flask of about 300 c.c. capacity, in which the concentration is continued, with the addition of 10 c.c. of sulphuric acid, until the water has been completely boiled off. A fragment of copper foil is then added and the experiment continued in accordance with the directions given in Chapter II.

• According to Blair, waters of great purity contain less than .06 part of organic nitrogen per 1,000,000 when estimated in this way, while waters containing .32 part per 1,000,000 are to be condemned.

Oxygen Absorbed.—As already stated, this process when taken in conjunction with the free and albuminoid ammonia gives valuable data upon which an opinion may be based. It gives the amount of organic matter in solution in terms of the oxygen required to oxidise it. Further, it enables us to distinguish between the readily oxidisable first decomposition products and the more complex organic bodies, since the former, at ordinary temperatures, are very rapidly oxidised and the latter only slowly. In contact with oxidisable matter potassium permanganate readily gives up its oxygen, especially if sulphuric acid be present, in accordance with the equation



• The completeness of the oxidation of the organic matter varies with the temperature, the process only approaching quantitative exactness at 100° C. It is therefore very necessary that standard directions should be followed or comparable results will not be obtained.

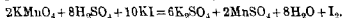
The particular temperature generally adopted is 80° F., in accordance with the recommendations of the Society of Public Analysts. The following solutions are necessary:—

- (1) Potassium permanganate, of which 1 c.c. contains 0.0001 grm. of available oxygen made by dissolving 0.396 grm. of pure potassium permanganate in a litre of distilled water, the solution will have the required strength.
- (2) Sodium thiosulphate, containing 1 grm. per litre of $Na_2S_2O_3$.
- (3) Potassium iodide solution of 10 per cent. strength.
- (4) Dilute sulphuric acid (1:3).
- (5) Starch solution made by making 2 grms. soluble starch into a thin cream with water and pouring, with stirring, into 100 c.c. of boiling distilled water.

The determination is carried out as follows:—

Oxygen absorbed in 15 minutes.—100 c.c. of the water are placed in a stoppered bottle of about 250 c.c. capacity and 100 c.c. of distilled water in a second exactly similar bottle. Ten cubic centimetres of potassium permanganate solution and 10 c.c. of dilute acid, both at a temperature

of 80° F., are now measured into the two bottles, which are then placed in a water-bath maintained at a temperature of 80° F. and allowed to stand for 15 minutes. If during this time the colour fades, a further 10 c.c. of permanganate is added to each bottle. At the end of the 15 minutes the bottles are well cooled and about 10 c.c. of potassium iodide solution are added to each bottle, when the unused permanganate will liberate its equivalent of iodine, as shown by the equation



The iodine dissolves in the excess of potassium iodide, forming a brown or yellow solution. The standard sodium thiosulphate solution is now run in from a burette, the stopper being carefully replaced and the bottle shaken after each addition until the colour has nearly disappeared. A few drops of starch solution are then added and the titration continued until the blue colour is just destroyed. From the difference between the number of c.c. of thiosulphate used by the distilled water and materials and by the sample, the amount of decomposed permanganate or absorbed oxygen can be calculated.

If x be the number of cubic centimetres of thiosulphate required by the blank experiment, i.e. by 10 c.c. of permanganate and acid, then x c.c. of thiosulphate are equivalent to 0.001 grm. oxygen, and 1 c.c. " " 0.001/ x grm. of oxygen. Now if y be the volume of thiosulphate used for the sample, then $(x - y) \times 0.001/x$ is the quantity of oxygen absorbed by the volume of the water taken in the experiment.

Oxygen Absorbed in Four Hours.—This is determined exactly as described above, only the bottle is allowed to stand in the water-bath for 4 hours instead of 15 minutes. It must be looked at from time to time and more permanganate added if the colour has faded. The above method may be much simplified without any loss of accuracy by titrating the permanganate directly with a standard solution of ammonium ferrous sulphate made by dissolving 4.90 grms. of the salt in 975 c.c. of water and adding 25 c.c. of sulphuric acid, making up to a litre when cold.

The solution should be kept in the dark and freshly made every 3 months. After the bottle containing the water and permanganate is taken from the bath the permanganate is titrated directly by adding the ammonium ferrous sulphate from a burette till the colour is just destroyed, or, in a better method, is added to each bottle in excess, say 20 c.c., and then titrated back with the permanganate solution till the pink colour is just permanent. The calculation is then carried out as follows:—

(a) Blank experiment—

20 c.c. of ammonium ferrous sulphate added.

10.0 c.c. permanganate solution required.

(b) Sample—

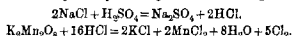
20 c.c. ammonium ferrous sulphate added.

10.5 c.c. permanganate used.

∴ Oxygen consumed = 5×0.001 grm.

A good water should not absorb more than 0.05 oxygen in 15 minutes nor more than .10 in 4 hours per 100,000 parts. The following modification of the absorbed oxygen test recommended by the Commission on Sewage Disposal gives valuable information in the case of polluted river water. The oxygen absorbed is determined as before, and a clean bottle is then completely filled with the water, stoppered, and placed in a cool incubator for a week, after which the oxygen absorbed is again measured. Badly polluted waters or those not properly aerated show an increase in oxygen absorbed after incubation.

The complete oxidation of the organic matter present in water generally requires a longer time than 4 hours at the temperature selected—80° F. The oxidation can be made much more rapid and complete by raising the temperature to the boiling point for 10 minutes. In the presence of much chloride the results are too high, owing to the fact that the liberated hydrochloric acid decomposes permanganate at a high temperature.



On this account, if the chlorides are high, an alkaline solution of permanganate is often used. The following method combines both determinations¹:—

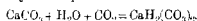
One hundred c.c. of water is placed in two conical flasks and 50 c.c. in two others. To one of the flasks containing 100 c.c. is added 10 c.c. of sulphuric acid (1 : 4), 5 c.c. being also added to one of the flasks containing 50 c.c. To the other two flasks are added 10 and 5 c.c. respectively of a saturated solution of sodium bicarbonate. Ten c.c. of a 0.5 per 1000 solution of permanganate is then added to each flask and the whole are boiled for 10 minutes. The flasks are then cooled and the alkaline solutions acidified with 20 and 10 c.c. respectively of sulphuric acid 1 : 2 solution. Ten c.c. of ammonium ferrous sulphate containing 10 grms. of sulphuric acid and 10 grms. of the salt per litre are introduced and the solution titrated with the permanganate until a faint pink colour is produced. The difference between the results of the 100 c.c. and 50 c.c. in each case gives the figure for the permanganate required for the oxidation of the organic matter in acid and alkaline solution respectively. The permanganate solution is titrated with pure crystallised oxalic acid.

There is much to be said for the double determination, since organic bodies often behave quite differently with acid and alkaline permanganate solutions. It must always be remembered that "absorbed oxygen" results cannot be compared with one another unless the methods used are identical in all respects. In stating results the method used should be specified, and that selected should, if possible, be the one in general use.

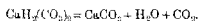
(6) **Hardness.**—Hardness in water is caused by the presence of salts of calcium and magnesium. That caused by the carbonates is termed "temporary" hardness, owing to the fact that it can be removed by boiling.

¹ *Water*, Permain and Moor, p. 72.

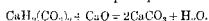
The carbonates of calcium and magnesium are not soluble in pure water, but water containing dissolved carbon dioxide acts upon them, producing soluble bicarbonates. Since all natural water contains carbon dioxide and percolates through strata containing carbonates of lime and magnesia, temporary hardness is practically never absent. The action of aqueous carbon dioxide is shown by the equation



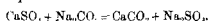
When water containing these acid carbonates is boiled they are decomposed with the evolution of carbon dioxide, and the normal carbonate is reprecipitated.



The bicarbonates may also be decomposed by lime, which withdraws and combines with the carbon dioxide and precipitates the original carbonates.

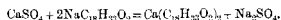


Permanent hardness, being due to sulphates and chlorides of calcium and magnesium, compounds which are directly soluble in water, is unaffected by boiling, and can only be removed by means of a chemical reagent which is capable of converting the soluble into insoluble compounds. Carbonate of soda is the commonest reagent for this purpose, which throws down an insoluble carbonate, in the absence of carbon dioxide, in accordance with the equation



Where permanent hardness is partly due to magnesium compounds the sodium carbonate must be used in conjunction with sufficient caustic lime or soda to throw down the magnesium as hydrate, since magnesium carbonate is not readily precipitated by sodium carbonate alone.

Estimation of Hardness.—Hardness in water may be estimated by taking advantage of the fact that calcium compounds decompose soap with the formation of an insoluble calcium compound.



A standard soap solution is made by dissolving 10 grms. of Castile soap in methylated spirit, filtering, and diluting to a litre. The strength should be such that 1 c.c. is equal to 1 milligramme of calcium carbonate. It is standardised as follows:—One grm. of Iceland spar is dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in water and made up to a litre with distilled water. Ten c.c. of this solution are then put into a stoppered bottle and made up to 100 c.c. with distilled water. A few drops of the soap solution are then added from a burette, the stopper replaced, and the bottle vigorously shaken. If, after standing for two minutes, there is no lather, more soap solution is added until a lather is produced which is permanent for two minutes. If the soap solution is of the right strength, the lather—permanent for two minutes—should be produced by 11 c.c.

In making tests, 50 c.c. of the water are placed in a stoppered bottle

holding about 150 c.c., and the soap solution added in quantities of 2 c.c. at a time. When the liquid shows signs of lathering, the bottle should be laid on its side, and the lather should remain as nearly as possible for 2 minutes. Great care should be taken to distinguish between the real soap lather and the scum given by magnesium salts. The results given by this method are not accurate if more than 10 c.c. of soap solution be used. In this case the water must be diluted and the operation recommenced. This is especially necessary when magnesium is present in any quantity, magnesium carbonate being decomposed by the soap solution with difficulty.

TABLE IIIA.—HARDNESS.
Parts of CaCO_3 per 100,000.

c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .	c.c. of Soap solution.	Parts of CaCO_3 .
0.7	.00	3.3	3.64	5.9	7.29	8.5	11.05	11.1	15.00	18.7	19.13		
.8	.16	4	.77	6.0	.43	.6	.20	.2	.16	.8	.29		
.9	.32	5	.90	.1	.57	.7	.35	.3	.32	.9	.44		
1.0	.48	6	4.03	2	.71	.8	.50	.4	.48	14.0	.60		
.1	.63	7	.16	.3	.86	.9	.65	.5	.63	.1	.76		
.2	.79	8	.29	.4	8.00	9.0	.80	.6	.79	.2	.92		
.3	.95	9	.43	.6	.14	.1	.95	.7	.95	.3	20.03		
.4	1.11	4.0	.57	.6	.29	.2	12.11	.8	16.11	.4	.24		
.5	.27	.1	.71	.7	.43	.3	.26	.9	.27	.5	.40		
.6	.43	.2	.86	.8	.57	.4	.41	12.0	.43	.6	.56		
.7	.56	3	5.00	.9	.71	.5	.56	.1	.59	.7	.71		
.8	.69	.4	.14	7.0	.86	.6	.71	.2	.75	.8	.87		
.9	.82	5	.29	.1	9.00	.7	.86	.3	.90	.9	21.03		
2.0	.95	.6	.43	.2	.14	.8	13.01	.4	17.06	15.0	.19		
.1	2.08	.7	.57	.3	.29	.9	.16	.5	.22	.1	.35		
.2	.21	.8	.71	.4	.43	10.0	.31	.6	.38	.2	.51		
.3	.34	.9	.86	.5	.57	.1	.46	.7	.54	.3	.68		
.4	.47	5.0	6.00	.6	.71	.2	.61	.8	.70	.4	.85		
.5	.60	.1	.14	.7	.86	.3	.76	.9	.86	.5	22.02		
.6	.73	.2	.29	.8	10.00	.4	.91	13.0	18.02	.6	.18		
.7	.86	.3	.43	.9	.15	.5	14.06	.1	.17	.7	.35		
.8	.99	.4	.57	8.0	.30	.6	.21	.2	.33	.8	.52		
.9	3.12	.5	.71	.1	.45	.7	.37	.3	.49	.9	.69		
3.0	.25	.6	.86	.2	.60	.8	.52	.4	.65	16.0	.86		
.1	.38	.7	7.00	.3	.75	.9	.68	.5	.81				
.2	.51	.8	.14	.4	.90	11.0	.84	.6	.97				

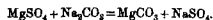
When this point is reached the whole of the salts producing hardness will have been decomposed, and by reference to Table IIIA. the amount of hardness can be immediately found. This number will indicate the total hardness of the sample. In order to determine the temporary hardness, 100 c.c. of the water are gently boiled for about three-quarters of an hour in order to expel carbon dioxide, and thus precipitate the magnesium and calcium carbonate in solution. It is then filtered into a 100 c.c. flask, the filter carefully washed, and the filtrate made up to the mark. Fifty c.c. of this filtrate are now treated with the

soap solution as before, and the hardness found by reference to the table. The permanent hardness of the water is thus found, and by deducting this number from the total found in the first part of the experiment the temporary hardness is obtained. There are many objections to the use of soap solution for determination of hardness, an important one, as already mentioned, being that if more than 10 c.c. of soap solution are required, the result will be inaccurate. The chief objection, however, is the difficulty in distinguishing between magnesium soaps and true lather. Hardness is now almost invariably estimated by Hehner's method, which is carried out as follows:—

Temporary Hardness.—One hundred c.c. of water are carefully titrated with decinormal acid and methyl orange, the latter substance not being affected by carbonic acid. Each cubic centimetre of decinormal acid corresponds to .005 part of calcium carbonate; hence, if 5 c.c. of acid were required, the temporary hardness expressed in terms of calcium carbonate would be $.005 \times 5$ in 100 c.c., or 25 parts per 100,000 of water.

Professor H. R. Procter, in the *Journal of the Soc. of Chem. Industry* for 15th January 1904, draws attention to the fact that when titrating hardness by Hehner's method, the end reaction with methyl orange is not sharp. He advocates the carrying out of a blank experiment side by side with the water under examination. This difficulty is overcome by Pfeifer and Wartha by the use of alizarin as indicator. The water is placed in a porcelain basin and the acid added until the violet changes to a distinct lemon yellow; at this point the liquid is brought to the boil, when on the escape of the carbonic acid the violet colour will return. This is destroyed by another drop of acid and the liquid again boiled, the operation being repeated till the violet colour no longer returns. Special stress is laid on the fact that Bohemian beakers give a very marked alkalinity to the solutions boiled in them.

Permanent Hardness (Hehner's Method).—One hundred c.c. of water are placed in a flask, in the neck of which is inserted a filter funnel to prevent undue loss by evaporation, 20 c.c. of $\frac{N}{10}$ sodium carbonate are added and the contents of the flask gently boiled for about an hour. Small quantities of distilled water may be added from time to time, if necessary. The liquid is then filtered into a beaker, and the filter washed with boiling distilled water until the last traces of sodium carbonate have been removed. The precipitated carbonates will now be all on the filter, and in addition to those producing temporary hardness will also include the equivalent of the permanent hardness decomposed by the carbonate of soda, as shown by the equation:—



The filtrate will contain the residue of the 20 c.c. of the sodium carbonate over and above that required for the decomposition of the permanent

hardness. A drop of methyl orange is now added and the sodium carbonate determined by titration with decinormal acid.

Suppose 14 c.c. of decinormal acid are required; then it is evident that 6 c.c. of decinormal carbonate of soda have been required to decompose the permanent hardness in 100 c.c. of water. Therefore the permanent hardness is six times 0.005 expressed as calcium carbonate, i.e. 30 parts per 100,000.

It has been pointed out that since magnesium carbonate is slightly soluble in water the results obtained by the above method are often too low.

Pfeifer and Wartha overcome this difficulty by using an equal mixture of $\frac{N}{10}$ sodium carbonate and sodim hydrate, instead of all sodium carbonate.

By this means the magnesia is precipitated as hydrate and not as carbonate, the hydrate being insoluble. The calcium is unacted upon by the sodium hydrate and is precipitated as carbonate, as before.

Pfeifer's Method of Determining Hardness. — By ordinary hardness determinations alone it is impossible to determine the quantities of the materials required for softening.

Pfeifer¹ determines these quantities in the following manner:—One hundred c.c. of water is neutralised with $\frac{N}{10}$ acid in the presence of alizarin in boiling solution, as described above. A known quantity of clear lime water (25 or 50 c.c.) is then measured into a 200 c.c. flask, and the hot neutralised solution poured in, rinsing and making up to 205 c.c. with boiling distilled water free from carbonic acid. The solution is then shaken and cooled, when it contracts to 200 c.c. Having allowed the precipitate to settle, 100 c.c. of the clear liquid are pipetted off and titrated with $\frac{N}{10}$ acid, using either phenolphthalein in the cold, or alizarin with boiling.

A volume of lime water equal to that used for the precipitation of the magnesia in the above experiment is then titrated with phenolphthalein as indicator. Deducting the $\frac{N}{10}$ acid required for the mixture of lime water and water from that used for the lime water alone, the difference multiplied by 5 gives the hardness due to magnesia in terms of milligrammes of CaCO_3 per 100,000, from which the actual Mg may be calculated by multiplying by 0.24 or MgO by 0.4.

The process depends upon the fact that Ca(OH)_2 will precipitate MgO , but has no action on lime salts.

If iron be present, it will, of course, be reckoned as magnesia, and should be determined colorimetrically by means of potassium thiocyanate and due allowance made for the quantity found.

¹ *J.S.C.I.*, 1904, p. 8.

It may be assumed that the iron is in the ferric state, in which case 0.24 part of Mg corresponds to 0.3733 of iron.

The quantities of the reagents required to soften the water may now be calculated from the formulæ¹ :—

$$\begin{cases} 5.6 (Ht + Hm) = \text{CaO required.} \\ 10.6 H_p = \text{Na}_2\text{CO}_3 \text{ (dry) required} \\ \text{or } 28.8 H_p = \text{Na}_2\text{CO}_3 \text{ crystals required.} \end{cases}$$

Ht in the formula signifies temporary and *H_p* permanent hardness, and *H_m* hardness due to magnesia, whether temporary or permanent.

The quantities are given in milligrammes per litre, grms. per cubic metre, or lbs. per 100,000 gallons of water to be treated.

If only temporary hardness is to be removed by liming alone, the quantity required is 5.6 (*Ht* + *H_m* - *H_p*) if *H_m* is greater than *H_p*, but if *H_m* be not greater than *H_p*, only the temporary hardness need be taken into account.

For softening with NaOH and Na₂CO₃ the formulæ are—

$$\begin{aligned} 8 (Ht + Hm) &= \text{NaOH required.} \\ \text{and } 10.6 (H_p - (Ht + Hm)) &= \text{Na}_2\text{CO}_3 \text{ required.}^2 \end{aligned}$$

If the water has less permanent hardness than the sum of the temporary and magnesia hardness, it cannot be completely softened in this way without leaving an excess of sodium carbonate in the water.

The determination of hardness is of great importance in a tannery. If a water containing much temporary hardness is used in any of the later stages of manufacture, the calcium carbonate will frequently be deposited in the tissue, giving the leather a hard feel when finished. This difficulty can be overcome by titrating the water as in the determination of temporary hardness by *Hegner's* method and adding to it in bulk the requisite quantity of acid necessary to keep the carbonate in solution. Acetic or lactic acid is preferable to a mineral acid for this purpose. The effect of hard waters upon the extraction of tanning materials has already been referred to. Table IV. shows the effect of temporary and permanent hardness on the extraction of tanning materials (*Nihoul, loc. cit.*).

Phosphates.—The presence of phosphates in water unless accounted for by the geological formation is always indicative of sewage pollution. They are detected by means of ammonium molybdate solution, which is prepared by adding 50 grms. of molybdic acid to 100 c.c. of water, and then mixing with 100 c.c. of ammonia solution of .88 sp. gr., and stirring until a clear solution is obtained. This solution is then poured quickly into 720 c.c. of nitric acid of 1.2 sp. gr., with continual stirring. After allowing the liquid thus obtained to stand for some hours, the clear solution is decanted

¹ Procter, *J.S.C.I.*, 1904, p. 10.

² These formulæ are only to be recommended when time will not allow of a gravimetric analysis, *c. p. 38.*

off for use. In the examination of water a litre is concentrated in the presence of nitric acid until its bulk is sufficiently small to enable it to be introduced into a platinum or porcelain dish. It is then evaporated to dryness on the water-bath to render the silica insoluble. The residue is extracted with dilute nitric acid, filtered, and concentrated to about 5 c.c., to which an equal volume of the molybdic solution is added. In the presence of phosphates a yellow coloration will be obtained, but if present in excessive quantities, a precipitate will be thrown down. The quantity of phosphoric acid in water is so small that it is quite useless to try to estimate it unless at least 2 litres of the water are evaporated; but the actual quantity present is not of so much importance, and it is usual merely to differentiate by the terms trace, distinct, and heavy traces.

TABLE IV.

Water Employed.	I.	II.	III.
Total Hardness,	21.84	23.12	26.28
Permanent Hardness,	8.76	10.28	14.62
Solids per litre,	910.8	812.0	1843.0
<i>Chestnut—</i>			
Organic Extract,	17.84	16.75	...
Tannin,	11.85	15.28	...
Non-Tannin Total,	7.96	9.16	...
Insoluble Matter,	69.10	70.11	...
<i>Sumach—</i>			
Organic Extract,	29.08	31.46	18.42
Tannin,	12.07	6.97	2.11
Non-Tannin Total,	23.69	32.89	26.56
Insoluble Matter,	55.61	51.10	62.72
<i>Valonia—</i>			
Organic Extract,	47.63	45.17	41.91
Tannin,	33.18	33.27	29.11
Non-Tannin Total,	19.15	17.71	20.66
Insoluble Matter,	33.19	34.75	36.19

Water Standards.—It is practically impossible to set up rigid standards of purity for waters which are capable of general application. Many attempts have been made, but they all fail to take the "local conditions" into account. There is, of course, never much doubt about water being free from pollution, but frequently it is a matter of the greatest difficulty to say, on general principles, that a water is contaminated with sewage pollution. In such cases recourse should be had to a bacteriological examination; in fact, this method of investigation should in all doubtful cases accompany chemical analysis. Table V. shows the quantities of the various constituents in parts per 100,000 usually found in the different classes of unfiltered natural waters. Any great rise in either of the figures, unless accounted for satisfactorily, indicates pollution.

TABLE V.

	Deep Well Water.	Surface and Subsoil Water.	River Water.
Total Solids,	16.00	20-50	20-50
Chlorine,	1.25	2-5	2-5
Nitrogen as Nitrate,	0.02	0.5-2.0	0.5-2.00
Free Ammonia,	0.005	0.005-0.025	0.025-0.10
Albuminoid Ammonia,	0.010	0.005-0.025	0.025-0.05

According to Wanklyn, standard waters may be classified as follows:—

Albuminoid Ammonia,	.005	great purity.
	.01	fair purity.
	more than .01	impure.

If organic nitrogen estimated by Kjeldahl's process be used as a means of classification, the following may be adopted:—

Less than	.006	great purity.
Between	.006 and .012	medium purity.
„	.012 and .032	suspicious (unless of peaty origin).
Above	.032	impure.

For oxygen absorbed the general standards are:—

Oxygen absorbed per 100,000 parts in three hours.		
	.1	great purity.
Between	.1 and .3	medium purity.
„	.3 and .4	doubtful.
Above	.4	impure.

In practice it is found that owing to differences in geological formations and other local conditions different standards are required for different localities. These, it is true, can only be set up for limited areas, but for all water within that area, are of the greatest service. In a certain thinly-populated area the author has made analyses of a large number of samples of water drawn from the same source in which the idea of pollution is absolutely precluded. All these have been found to be of remarkable constant composition, the variation over a period of about four years being shown by the following table, the figures in which represent parts per 100,000:—

TABLE VI.

	I.	II.	III.	IV.	V.	VI.
Total Solids,	35.6	38.6	39.6	35.6	38.2	35.3
Chlorides,	1.47	2.10	1.24	1.7	1.4	1.75
Nitrates,61	.37	.27	.50	trace	.15
Free Ammonia,002	.007	.002	.016	.005	.000
Alb. „010	.008	.000	.012	.016	.018
Temp. hardness,	25.5	...	25.5	25.0	26.0	26.0
Perman. „	1.5	...	1.5	2.0	2.0	1.5

Since these figures all represent waters of known organic purity (proved also by bacteriological analysis in each case), they may be reasonably taken as standards for the district, and any water that fails to reach this standard may be safely condemned.

The following from same district fail to reach standard:—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Chlorides,	4·84	3·85	6·89	3·18	7·07	3·18
Nitrates,	2·69	1·83	4·30	2·15	21·5	7·52
Free Ammonia,	·000	·015	·000	·012	·000	0·000
Albuminoid Ammonia,	·011	·016	·009	·029	·013	·014

A further example of the difficulty attending the use of rigid standards may be quoted.

W. W. Fisher points out¹ several cases in which waters not necessarily contaminated may contain abnormal chlorides. Waters of this type are obtained from the chalk beneath the London clay and contain only mere traces of lime and magnesia as carbonates, while considerable quantities of alkaline salts, mainly consisting of sodium chloride, sulphate, and carbonate are present, rendering the water soft and alkaline.

Poisonous Metals.—These are rarely found in natural waters, but are sometimes to be detected in water after standing in contact with metal pipes, particularly if it be devoid of hardness. When present they will be found by evaporating a litre of water to dryness with a little dilute nitric acid, extracting with water and filtering into a Nessler cylinder, making up to 50 c.c. Sulphuretted hydrogen is then passed through the solution, and in the presence of lead or copper a brownish coloration will be produced. The quantity of the metal present may be approximately estimated colorimetrically by matching the colour with a standard solution of lead acetate containing ·0001 gm. of lead per cubic centimetre. An instance of barium in solution in a natural water is quoted by White, *Analyst*, 1899, p. 67, in sufficient quantity to estimate it without concentration by acidifying with dilute hydrochloric acid and precipitating with very dilute sulphuric acid.

Ultimate Analysis of the Dissolved Solids.—From half a litre to a litre of water, according to the quantity of total solids present, is acidified with HCl and evaporated to dryness in a large platinum dish on the water-bath. It is then moistened with dilute hydrochloric acid and again thoroughly dried to decompose the last traces of silicic acid. Upon extraction with dilute hydrochloric acid the silica remains insoluble and is carefully filtered off, washed, and dried. When dry the filter is folded and placed in a weighed platinum dish and ignited, the precipitate being far

¹ *Analyst*, 1907, p. 202.

too small to detach. Deducting the weight of the filter ash we obtain directly the weight of the silica.

Iron and Alumina.—The filtrate is rendered alkaline with ammonia and placed upon the water-bath for some time to complete the precipitation of the ferric hydrate and alumina. The precipitate is then filtered off, washed, dried, and weighed in the same manner as the silica. The amount is generally so small that a separation is unnecessary.

The iron is best determined on a fresh portion of water by evaporating to dryness with a little nitric acid, extracting the solids well with water and adding to the solution, in a Nessler cylinder, a few drops of potassium ferrocyanide solution, when a blue solution will be produced proportional in depth to the quantity of iron present. A standard solution of iron is made up so that each cubic centimetre is equivalent to .001 gm. of ferric oxide. This is made by weighing the necessary quantity of pure iron oxide, dissolving it in aqua regia, evaporating to dryness to expel chlorine, and finally making up to a litre with dilute acid. A known volume of this solution is run from a burette into a Nessler cylinder, water added until the volume is the same as that in the first, and a few drops of potassium ferrocyanide solution as before. The columns are then compared by standing the cylinder on a white tile and looking vertically down through the liquids. If they are of the same tint the two liquids contain equal quantities of iron, and hence that in the first is equal to the amount contained in the volume of iron solution placed in the second. If the tints are not identical, further experiments must be made with varying quantities of iron solution until the required volume is found.

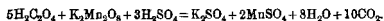
Lime.—The filtrate from the iron and alumina precipitate is concentrated by gently boiling in a beaker on a sand-bath until it occupies about 100 c.c. A little more ammonia is now added, and about 2 grms. of finely powdered ammonium oxalate is gradually stirred in, the beaker being removed from the sand-bath for this purpose. It is then replaced on the sand-bath and allowed to boil gently for a minute, after which it is removed and the precipitate allowed to settle. After about half an hour the clear liquid is carefully decanted on to a hard filter paper (Schleicher and Schüll, No. 590), as much of the precipitate as possible being left in the beaker. About 25 c.c. of hot distilled water are now poured into the beaker and the precipitate well stirred, and when it has settled the liquid is decanted as before on to the filter. This is continued until the washings no longer give any turbidity with silver nitrate acidified with nitric acid. The precipitate is now washed on to the filter paper with a stream of hot distilled water and dried in the water oven. When dry the precipitate is carefully removed from the filter on to a piece of black glazed paper and covered with a funnel while the paper is being incinerated in a weighed platinum crucible. To remove the precipitate lay the filter paper carefully on the glazed paper and press down the upper half till it lies perfectly flat. Then holding it in this position with the left hand, rub the upper surface

with the fingers of the right. In this way nearly the whole of the precipitate will be detached; and if the filter be now held by the apex of the cone and very carefully inverted it will be transferred to the glazed paper without loss. Next fold the filter paper into a small cone and wrap it with platinum wire. Hold the cone above the crucible standing on a piece of glazed paper and burn it as completely as possible with a bunsen flame until it drops into the crucible beneath. By means of a camel's hair brush any particles of ash that may have dropped on the paper are brushed into the crucible, the contents of which are then ignited in a bunsen flame until quite white. The precipitate from the glazed paper is now gently poured into the crucible, the brush being used if necessary to remove the last traces. There are now three methods of treating the precipitate.

(1) *As Calcium Carbonate.*—When the weight of the precipitate exceeds half a gramme this will be the best method to employ. The crucible is gently ignited at a dull red heat till the oxalate has been converted into carbonate. As in all probability some of the carbonate will have been over-ignited and thereby changed to lime, a little finely powdered carbonate of ammonium is now added to the crucible and gentle heat applied till the excess is completely driven off. The crucible is then cooled and weighed, and the treatment with ammonium carbonate repeated till the weight is constant.

(2) *As Lime.*—When the weight of the precipitate is small, strong ignition of the oxide is the better method. The crucible is heated as strongly as possible with a blowpipe flame for about ten minutes, cooled in a desiccator and weighed. It is then heated again for a further ten minutes and weighed, the process being continued until there is no further loss in weight.

(3) *Estimation of Lime by Means of Standard Permanganate.*—When the precipitated oxalate has been transferred to the filter paper in the manner described above, it may be more rapidly estimated by decomposing it with sulphuric acid and titrating the liberated oxalic acid with potassium permanganate. The equation is



If this method be adopted the filter paper is perforated by means of a glass rod drawn out to a fine point and the whole of the precipitate washed through into a beaker with a stream of hot distilled water. A few cubic centimetres of dilute sulphuric acid are next added to liberate the oxalic acid. The temperature of the solution is now raised to about 60° C., and standard permanganate solution is run in from a burette until a permanent pink colour is obtained. Each c.c. of permanganate solution being equivalent to 0.45 gm. of oxalic acid, the quantity of calcium or lime present in the beaker can be calculated.

Magnesium.—The filtrate from the calcium oxalate precipitate is evaporated to dryness in a platinum dish on a water-bath, the last traces

of water being expelled by carefully heating in an air-bath at a temperature of about 120° C. The dish is now covered with a clock glass to prevent loss by spitting, and is gently heated over a flame until all the ammonium salts have been expelled. The residue is dissolved in dilute hydrochloric acid, and, if necessary, filtered. To the clear solution a moderate excess of ammonia and sodium phosphate is added, the ammonia being necessary since the precipitated phosphate is slightly soluble in water, but not in ammonia solution. Stir the liquid briskly with a glass rod, taking care not to rub the sides of the beaker, cover it with a clock glass and allow it to stand over night. This delay may be dispensed with if the precipitation be carried out in a stoppered bottle and the mixture thoroughly shaken for about a quarter of an hour. When the precipitation is complete, decant the clear liquid through a filter paper and wash the precipitate by decantation with 1 : 3 ammonia water. The washing is continued until the filtrate, when acidified with nitric acid, gives no precipitate with silver nitrate. The precipitate is now transferred to a filter and dried. When dry it is detached as completely as possible from the filter and transferred to a weighed platinum crucible, the paper being separately burnt and added thereto.

The crucible is now ignited for about twenty minutes to convert the magnesium ammonium phosphate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) into pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), the weight of which multiplied by $\cdot 3604$ gives the quantity of magnesia (MgO) in the precipitate. The total volume of the washings is measured and 1 mgm. added to the weight of the precipitate for each 50 c.c. This is necessary, since the magnesium phosphate is slightly soluble in the ammonia water used.

Alkalis.—A litre of water is concentrated to about 100 c.c. The sulphates are then precipitated by means of barium chloride solution and filtered off. The filtrate is boiled with milk of lime to precipitate iron and magnesium. These are filtered off, and the barium and calcium in the filtrate are now removed by the addition of ammonia, ammonium carbonate, and a little ammonium oxalate. Having ensured the complete precipitation of these metals, filter, make faintly acid with HCl , and evaporate the filtrate to dryness in a weighed platinum dish. Now gently ignite it until all the ammonium salts are expelled, then weigh the residue, which will consist of the chlorides of sodium and potassium, removing the last traces of water and free acid by gentle ignition.

If it be necessary to estimate the sodium and potassium separately, dissolve the residue in a little distilled water and evaporate to dryness again on the water-bath and then gently ignite to expel the last traces of acid. Now take up again with distilled water, and by means of standard silver nitrate solution find the weight of chlorine contained in the mixed chlorides. From these data the alkalis may be calculated. The following example from Whiteley's *Chemical Calculations* will make the method plain :—

The mixed chlorides weighed 1.449 grms. and the chlorine content

found by titration was 0.7739. If the whole of the chlorine found had been present as KCl, there would have been 1.6241 grms. of chloride. The difference between this weight and the weight actually found is 0.1751 grm. Now

The difference between the molecular weights of KCl and NaCl	:	the deficiency in weight found	::	the molecular weight of NaCl	:	x
--	---	--------------------------------------	----	------------------------------------	---	---

where x = the NaCl present in the mixed chlorides.

$$\therefore 16 : 0.1751 :: 58.5 : x,$$

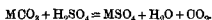
$$\text{i.e. } x = .6402$$

= weight of NaCl in the mixed chlorides.

The potash may also be determined by converting the residue into the double chloride $\text{PtCl}_2 \cdot 2\text{KCl}$. The residue is dissolved in a few cubic centimetres of water and excess of platinum chloride is added. The solution is evaporated on the water-bath till nearly dry, and alcohol is then added to dissolve out the excess of platinum chloride and the sodium compound. The insoluble potassium salt may be readily washed with alcohol by decantation till the washings are quite colourless, after which it is washed into a weighed dish or filter paper, dried and weighed. After weighing, the precipitate is ignited and the residue of metallic platinum weighed, and from these data the weight of the potash present can be calculated. The sodium is obtained by difference.

Sulphates.—Two hundred c.c. of the water are filtered and acidified with dilute hydrochloric acid and brought to the boil in a beaker. Sufficient barium chloride is now added to precipitate the sulphates and the contents of the beaker boiled gently for about five minutes on a sand-bath in order to render the fine precipitate easier to filter. The precipitated barium sulphate is now allowed to settle and the clear supernatant liquid carefully decanted on to a hard filter paper (Schleicher and Schüll, No. 590). The precipitate is washed as completely as possible by decantation with distilled water and is finally transferred to the filter with a fine jet of hot water. It is then dried and ignited and weighed in the usual way. The weight of the precipitate multiplied by .3433 gives the quantity of SO_3 present.

Carbon Dioxide.—The quantity of combined carbon dioxide as CO_2 may be calculated from the temporary hardness, as determined by Hehner's method from the equation



Thus 44 parts of CO_2 are equal to 98 of sulphuric acid, or to 100 parts of temporary hardness expressed as calcium carbonate, hence every part of temporary hardness found will correspond to 0.44 part of CO_2 .

Statement of Results.—We have now arrived at a knowledge of the quantities of the various inorganic constituents of the water, but as yet we know nothing as to the actual form of the combination of the acids and bases. These may, however, be calculated from the data at our disposal if we remember the relative affinities of the acids and bases with which we are dealing.

The method adopted is best explained by a concrete example.

A water gave the following result upon analysis:—

TABLE VII.

Chlorine,	5.25	} parts per 100,000.
Calcium,	25.17	
Magnesium,	3.15	
Sodium,	2.00	
Sulphuric Acid (SO ₄),	9.30	
Carbonic Acid (CO ₂),	37.95	

First we assume that sodium will be in combination with chlorine. Now 2 parts of sodium will combine with $\frac{35.5 \times 2}{23}$, i.e. 3.08 parts of chlorine, giving rise to 5.08 parts of sodium chloride. There are 5.25 – 3.08, i.e. 2.17 parts of chlorine left over, and these will next combine with magnesium. Now 2.17 parts of chlorine will combine with $\frac{24 \times 2.17}{71}$, i.e. 0.74 of magnesium, giving 2.91 parts of magnesium chloride.

We next take the sulphuric acid, which will combine with the calcium, and any excess that remains with magnesium. Now 9.30 parts of SO₄ will combine with $\frac{40 \times 9.30}{96}$, i.e. 3.87 parts of calcium giving 13.17 parts of calcium sulphate. We have left 21.3 parts of calcium which will be in combination with carbonic acid, and will require $\frac{21.3 \times 60}{40}$, i.e. 31.95 parts giving 53.25 parts of calcium carbonate. There are now left 2.41 parts of magnesium and 6.00 parts of carbonic acid (CO₂) which will combine, giving 8.4 parts of magnesium carbonate. Thus we now have the following results:—

TABLE VIII.

Sodium Chloride,	5.08
Magnesium Chloride,	2.91
Calcium Sulphate,	13.17
Calcium Carbonate,	53.25
Magnesium Carbonate,	8.40

However, if Pfeifer's method of estimating magnesium be employed, the method of working out the above figures becomes much simplified.

Bacteriological examination of water for tanning purposes. Practically the only determination necessary is a measurement of the number of quefying organisms present—that is, those that are able to attack and eptonise gelatine. For this purpose a tube of sterilised gelatine is melted. With a finely graduated sterilised pipette a definite quantity, say 0.25 c.c., of the water is then added to the melted gelatine, the plug replaced, and, after mixing, the contents of the tube are poured into a sterile Petri dish and allowed to set. The dish is then kept in an incubator at 20° C. or in a cool place for a few days and the number of liquefying colonies carefully

CHAPTER V.

EFFLUENTS.

TAN-YARD effluents, in addition to the usual organic matter, will also be liable to contain such bodies as excess of chromate, sodium thiosulphate, tannic acid, arsenic, antimony, acids, etc. The routine analysis of an effluent includes—

Total Solids.	Oxygen Absorbed.
Suspended Matter.	Ammonia.
Chlorine.	

These are determined by the methods already described under water analysis, except that in the case of ammonia a smaller volume of water must be used than 500 c.c.

The effluent should be diluted with distilled ammonia-free water and the dilution allowed for in the calculation of the results. A little of the effluent should be tested first of all with Nessler solution and the quantity taken for analysis varied according to the coloration obtained. In general it is safer to distil off 200 c.c., mix thoroughly, and nesslerise 50 c.c. When the free ammonia is very high the following alternative method may be used:—Place from 1 to 5 c.c. of the liquid in a 100 c.c. flask and make up to the mark and determine the free ammonia directly in an aliquot portion of this liquid by means of Nessler solution. Then estimate the total ammonia by distilling a measured volume of the diluted effluent with alkaline permanganate, and to obtain the albuminoid deduct the free ammonia found in the first experiment.

Dissolved Gases.—Although insufficient aeration of water is no criterion of pollution, yet it is evident that unless it be well aerated there can be little self-purification. Hence it is frequently necessary to estimate the quantities of dissolved gases in water. These may readily be extracted by means of an apparatus (fig. 9) described by Harvey in the *Analyst* for 1894, p. 121.

It consists of a globular, spindle-shaped vessel (A), $3\frac{1}{4}$ to $3\frac{1}{2}$ in. in diameter, with two tapering necks, the total length being 13 to 14 in. The upper neck is somewhat larger than the lower, which is narrow and

cylindrical, and both end in a capillary bore with swollen tip, for rubber connections. To the upper extremity a short length of small-bore pressure tubing is securely tied and furnished with a screw clip (B), and leads to a nitrometer (F). The lower end is connected by means of pressure tubing to a movable reservoir (D).

The apparatus is used in the following manner:—

First, the exact capacity of the vessel is obtained once for all. It is then filled with the water to be analysed, and screw clamp (B) closed. The vessel is then carefully placed in a tin water-bath (C), 6 in. diameter, 7 in. high, standing on legs 12 in. high, by means of a perforated bung at G, and so arranged that, while the lower stem of the spindle projects 2 in. below the bottom, the globular part is immersed in the bath itself.

The clamp (B) is now opened, and about one-third of the water allowed to run out into a measured vessel. This volume deducted from the capacity

of the globe when full gives the amount experimented upon.

The lower end of the spindle is now joined to the reservoir (D) with about 2 ft. of pressure tubing.

Clean mercury is then poured into the reservoir, the clamp (B) opened, and the air expelled, the water being allowed to follow as far as the upper end of the tube (E). The clamp is now closed again. An ordinary nitrometer, containing mercury (F), is now connected at F, the mercury being forced to the end of the capillary tube before making the connection. The reservoir is now lowered and the clamp carefully opened, in order to draw in sufficient mercury to reach the

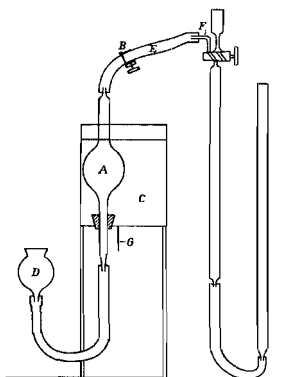


FIG. 9.

lower end of the upper capillary tube. The clamp is then closed and the water-bath filled with cold water and heat applied. To prevent the flame injuring the lower end of the spindle, a metal curtain (G) is riveted to the bottom of the bath so as to screen the glass from the flame, the bung being also at one corner of the bath.

Under the diminished pressure, the water in the reservoir soon begins to boil vigorously, without bumping, the expelled gases collecting in the upper stem. After about two hours' boiling, during which time the process requires but little attention, the reservoir may be raised, the clamp (B) opened and the gases passed into the nitrometer, taking care

not to let the "following water" rise as far as the capillary part of the spindle. The clamp is again closed, and the operation continued, until no more gas is expelled. The reservoir is then raised, and the residual gas driven completely into the nitrometer, the "following water" being allowed this time to go as far as the nitrometer tap.

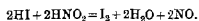
The apparatus is now disconnected from the nitrometer, and the contents of the latter, after cooling, are measured.

The approximate proportions of carbonic acid, oxygen, and nitrogen present may be determined in the following way:—After measuring the gas a little 50 per cent. sodium hydrate solution is drawn in from the cup and agitated with the gas in the nitrometer. After a few minutes the levels of the mercury are adjusted and the decrease in volume due to the absorption of the carbonic acid noted. A solution of pyrogallic acid in sodium hydrate is now introduced to absorb the oxygen, the residue, after reading the diminution in volume, being nitrogen.

Frequently it is only necessary to estimate dissolved oxygen, in which case a simpler method than the above may be used. The following is the best for the purpose:—

*Thresh's Method.*¹—This depends upon the fact that when sulphuric acid and potassium iodide are added to a water containing a solution of a nitrite, the amount of iodine liberated varies with the length of time during which it is exposed to the air.

If air be excluded there is no increase in the amount of iodine liberated after the first few minutes. If the water is free from dissolved oxygen, and the experiment carried out in an atmosphere of coal gas, iodine is liberated in accordance with the equation—



In the presence of oxygen the nitric oxide thus formed acts as an oxygen carrier, and is thus able to affect the decomposition of a larger quantity of iodide.

The following reagents are required:—

- (1) Solution of sodium nitrite and potassium iodide.

Sodium nitrite,	0.5 grm.
Potassium iodide,	20.0 grms.
Distilled water,	100 c.c.
- (2) Dilute sulphuric acid (1 in 3).
- (3) Standard solution of sodium thiosulphate.

Pure thiosulphate,	7.75 grms.
Water,	1000 c.c.

 (1 c.c. \approx 0.25 milligramme of O.)
- (4) A clear, fresh solution of starch.

¹ Fermin and Moor, *Analysis of Water*, p. 92.

The apparatus (fig. 10) consists of a wide-mouthed bottle of about 500 c.c. capacity, closed by a rubber bung, through which pass:

- (1) A tube drawn out to a rather fine point at the lower end, the upper being connected with a burette containing the thiosulphate.
- (2) A stoppered separating funnel.
- (3) A tube which can be attached to the gas supply.
- (4) An exit tube for the gas, of such a length that the end can be made to fit into the neck of the separating funnel.

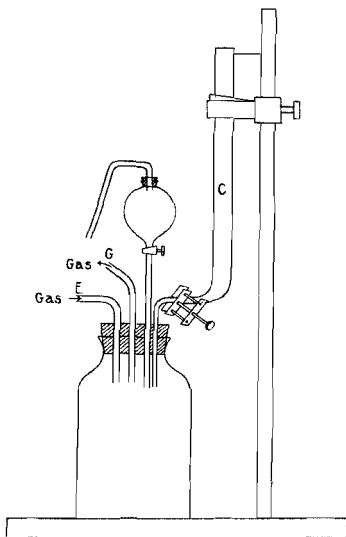


FIG. 10.

Estimation of the Dissolved Oxygen.—Fill the burette (C) with the standard thiosulphate, and connect the tube (E) to the gas supply.

Fill the separating funnel—the capacity of which has been previously accurately determined—with the sample of water to be examined, then add 1 c.c. of the solution of sodium nitrite and potassium iodide, and 1 c.c. of the standard acid. The pipette must be held vertically, the end reaching nearly to the bottom of the funnel, in which case the two solutions, being much denser than the water, immediately sink to the bottom.

Replace the stopper as quickly as possible, thus displacing a little of the water, but including no air. The funnel is then inverted to mix the contents thoroughly, and placed in its proper hole in the bung of the bottle. After about twenty minutes the action will be complete. Coal gas is then rapidly passed through the bottle and ignited at the exit tube (G). Extinguish the flame, remove the stopper from the funnel, and replace by the cork at the end of G. The sample in the separating funnel is now allowed to run into the bottle, the tap shut off, the tube (G) disconnected from the funnel, and the gas regulated so that it burns with only a small flame at the mouth of the exit tube.

The standard thiosulphate is now run in until the colour is nearly discharged. At this point a little starch (1 c.c.) is pipetted into the funnel and then run into the bottle. Continue the titration with the thiosulphate till the blue colour produced by the iodide of starch is completely destroyed. After a few minutes a little of it returns, due to the dissolved oxygen in the thiosulphate solution, etc. 0.05 to 0.1 c.c. more thiosulphate must be added to effect the final discharge. Note carefully the amount of standard solution used. This will represent (a) the oxygen dissolved in the water examined; + (b) the nitrite in 1 c.c. of the solution used, and the oxygen in the acid and starch solution; + (c) the oxygen dissolved in the thiosulphate solution.

To find the value of *a* it is necessary to know the values of *b* and *c*.

To find the value of *b*.—Complete a titration, as described above, and then by means of the funnel introduce 5 c.c. of the nitrite solution and starch. Allow to stand, and titrate. One-fifth of the thiosulphate used will be the value required.

To find the value of *c*.—This correction is a small one, and is determined with sufficient accuracy, if we assume that the thiosulphate normally contains as much oxygen dissolved in it as distilled water at the same temperature.

Complete a determination as described above, and through the funnel drop in 10 to 20 c.c. of distilled water. Allow to stand and titrate. A tenth or a twentieth of the solution used will represent the correction for each c.c. of the thiosulphate used.

Let this volume be *d*.

e be the number of c.c. of thiosulphate used.

f be the capacity of the funnel, less 2 c.c. the volume of the reagents added.

g the amount of oxygen in milligrammes dissolved in one litre of the water.

Then

$$g = \frac{1000}{4f} (e - b - ed).$$

With a funnel to hold exactly 250 c.c. (the most convenient quantity to use) $\frac{1000}{4f}$ becomes unity and

$$g = e - b - ed.$$

to be tested by the hide-powder method, but this will rarely be possible, and the presence of acid would render the method impossible. Titration with permanganate obviously cannot be employed, since the water contains other readily oxidisable organic matter, besides tannin.

Arsenic and antimony, if present, may be estimated as follows:—

Arsenic.—100 c.c. of the effluent are concentrated to 25 c.c. and then boiled with about half a gramme of potassium metabisulphate and a little sulphuric acid to ensure complete reduction of arsenates. After expelling the sulphur dioxide the liquid is then introduced into the inner cell of an electrolytic apparatus or other form of Marsh's apparatus. A suitable form of electrolytic apparatus is shown in figs. 11 and 12 (Trotman, *J.S.C.I.*, 1904, 177).

It consists of a double electrolytic cell, the inner portion of which is provided with a delivery tube carrying a drying tube and a drawn-out piece of combustion tube for the deposition of the arsenic. The drying tube is filled with calcium chloride and lead acetate paper, and the bottom of the tube is covered with a parchment diaphragm, which must be tested to ensure freedom from arsenic. The upper end of the inner cell is fitted with a rubber bung, through which pass an electrode which forms the cathode (made of arsenic-free lead)

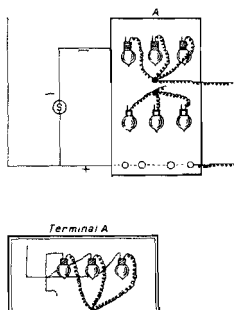


FIG. 12.

and a tap funnel for the introduction of the liquids to be tested. The outer cell stands in a dish of water to keep the apparatus cool. The inner cell is surrounded by a circular electrode, also made of lead, which is connected with the anode. The electric current is obtained from the main supply by means of a rheostat, which may be made of incandescent lamps arranged so that they are parallel to each other, but in series with the cell. A current of about 5 amperes is required, and sufficient lamps must be used to obtain this. The apparatus having been thoroughly washed, the outer cell is filled with dilute sulphuric acid (about 10 per cent.). Twenty-five c.c. of dilute acid, or sufficient to cover the enlarged portion of the cathode, are introduced through the funnel, and the current passed through for a few minutes to expel air. The rate of flow of the hydrogen should be sufficient to produce a flame of about 3 mm. As soon as the air has all been expelled a small bunsen burner is placed beneath the delivery tube at the point where the capillary commences, and the current is continued for about 20 minutes. If at the end of this time no deposit of arsenic is obtained, the purity of the

materials used is established. The solution to be tested for arsenic is now introduced through the tap funnel, and if there is any tendency to froth, a few drops of amyl alcohol may also be added. The current is continued for 30 to 40 minutes, at the end of which time all the arsenic will have been expelled as arsenuretted hydrogen. The arsenuretted hydrogen is decomposed as it passes over the heated portion of the capillary, the arsenic being deposited as a metallic mirror. The quantity of arsenic present is estimated by comparison with a set of similar standard mirrors made with known quantities of arsenious oxide.

Preparation of Standard Mirrors.—1 of a gramme of pure dry arsenious oxide is dissolved in sodium carbonate and made up to a litre. If 100 c.c. of this solution be diluted to a litre, each c.c. will contain 0.01 of a milligramme. This is a suitable strength of solution for preparing standard mirrors.

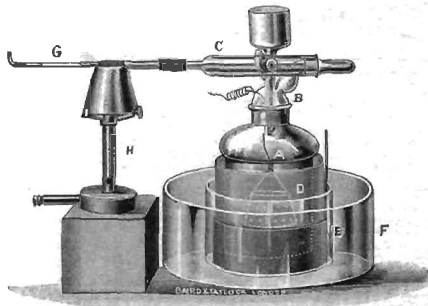


FIG. 13.

In preparing standard mirrors the experiment is carried out exactly as in making the above test, using definite volumes of the arsenious oxide solution corresponding to 0.01 to 0.10 milligramme of arsenious oxide. Fig. 13 shows a form of electrolytic apparatus recommended by the Commission on Arsenic in brewing materials in which the electrodes are of platinum and all the joints glass.

If an electric current is not available the hydrogen may be generated from zinc and sulphuric or hydrochloric acid. The apparatus required consists of a wide-mouthed bottle of about 250 c.c. capacity, which is fitted with a rubber bung through which pass a tap funnel and delivery tube with drying tube, as used in the electrolytic estimation.

The test is performed by placing 5 grms. of arsenic-free zinc in the bottle and then adding dilute arsenic-free acid together with a drop of copper sulphate solution. The hydrogen is allowed to escape until all

the air is expelled from the apparatus, after which the purity of the material is tested as before. The liquid to be tested is introduced through the tap funnel and the deposit of arsenic obtained and compared with a standard mirror as before. The objection to this method is that pure zinc is sometimes insensitive to arsenic, and its sensitivity should therefore always be proved before use. In the presence of much organic matter the efficiency of the method is considerably impaired.

Chromates and Chromium Compounds.—A considerable volume of the liquid should be acidified and concentrated to a small bulk. It is then treated with a suitable reducing agent, such as sugar or preferably metabisulphite of soda. After boiling, excess of ammonia is added, the liquid reboiled and the precipitated oxides filtered off and washed. They are then transferred to a beaker and treated with sodium peroxide and boiled for about half an hour to remove all traces of hydrogen peroxide, after which the bichromate is titrated in the ordinary way with sodium thiosulphate.

Unless subjected to some suitable treatment, tan-yard effluents will always contain considerable quantities of dissolved skin substance, lime, lime soap, grease, etc.

Free grease may be estimated by shaking with petrol in a separating funnel, while if the effluent be boiled with hydrochloric acid, soaps will be decomposed and the fatty acids may also be extracted and weighed.

Dissolved skin substance may be deduced from a determination of total nitrogen, the liquor being acidified with sulphuric acid before concentration.

Treatment of Waste and Effluents.—Tannery waste and effluents are treated in precipitating tanks and the clear liquor passed through coke filters. The sludge collected from the settling tanks is usually unsaleable, although it is of undoubted manurial value. It frequently contains a considerable quantity of recoverable grease, and it should be periodically examined for this constituent. In many cases it is well worth recovering. Thus, in one case known to the author, the scum floating on the surface of a settling tank was found to contain 48 lbs. of free grease per ton, while by breaking up the lime soaps with acid the yield was considerably increased. The recovery of waste is becoming increasingly important and should never be neglected.

Standard of Purity for Effluents.—These differ in different localities, but it may be taken as a general rule that no effluent is fit to be discharged into a stream which contains more than 0.10 part of albuminoid ammonia per 100,000. It should also be devoid of free alkali or acid and not contain sufficient arsenic or other poisonous ingredient to be dangerous to cattle drinking from the stream into which it is discharged.

The oxygen absorbed in five minutes should not be more than 0.05 per 100,000 parts, and should not increase after incubation at 20° C. for seven days.

CHAPTER VI.

DEPILATION.

Depilation is the process of removing the hair from a hide before tanning and follows immediately upon the softening and cleansing process. It is accomplished either by keeping the hides in a warm damp place till natural fermentation sets in or by the use of certain chemical substances. By far the most important of these is lime, although other alkalis (such as soda and potash) and various sulphides are also used. The analysis and chief characteristics of the various depilants are indicated in the following paragraphs.

Lime.—Commercial lime is subject to a great deal of variation chiefly owing either to under or over kilning, and since damage to skins may easily be caused by unsuitable limes they should invariably be carefully analysed. A good lime should contain from 90–96 per cent. of available lime and not more than 2 per cent. of magnesia. The presence of much magnesia causes very slow slaking, and hence small lumps of unslaked material often become caught in the hide and burn it. Limes containing much silica or carbonate (indicating incomplete burning) should be rejected. Any considerable quantity of iron is also objectionable, as any trace of iron left in the skin would subsequently combine with tannins and cause discoloration of the skin during tanning. The following examples of good and bad limes will illustrate these points:—

(1) *Bad Limes.*¹

TABLE X.

	(1)	(2)
Silica and Insoluble Matter,	17.70	1.88
Iron Oxide,	6.42	4.00
Lime,	49.86	55.97
Calcium Carbonate,	14.21	1.50
Calcium Sulphate,	3.01	0.91
Calcium Chloride,	0.38	...
Magnesia,	2.09	30.44
Moisture by Difference,	5.58	5.80
Organic Matter,	0.60	...
	100.00	100.00

No. 1 is remarkable for the deficiency in available lime and the presence of so large a quantity of iron and silica.

The second sample is practically a hydraulic lime owing to the presence of so large a percentage of magnesia. It would slake very slowly and undoubtedly cause damage to the hides.

(2) *Good Lime.*

TABLE XI.

Lime,	94.29
Iron Oxide,	0.17
Silica,	0.51
Magnesia,	0.05
Calcium Carbonate,	1.06
Calcium Sulphate,	1.96
Organic Matter, }	1.97
Moisture, }	
	100.00

Analysis of Lime.—In order to obtain a representative sample a considerable quantity should be finely powdered and preserved in a stoppered bottle. The following determinations are usually made if a complete analysis be required.

Matter Insoluble in Hydrochloric Acid (chiefly silica).—About 5 grms.

the finely powdered sample are weighed into a porcelain dish, to which is added 25 c.c. of strong hydrochloric acid. The dish is then covered with an inverted funnel and boiled gently on a sand-bath for half an hour, after which the funnel is carefully washed out with distilled water and the contents of the dish evaporated to dryness on the water-bath.

The residue is now taken up with dilute hydrochloric acid and filtered into a 250 c.c. flask, the insoluble matter being collected and washed till free from acid. The insoluble residue may consist of silica, some iron, and calcium silicate. It is dried in the water oven, ignited, and weighed. The filtrate is made up to 250 c.c.

Determination of Iron, Alumina, Lime and Magnesia.—25 c.c. (5 original sample) are withdrawn by a pipette, placed in a beaker, diluted with water and precipitated with excess of ammonia with the addition of a few ammonium chloride. After gently boiling for a few minutes the precipitate, consisting of oxides of iron and aluminium if present, is filtered off, washed, dried and weighed. It will generally be sufficient to weigh them together, but if it is desired to separate them, the precipitate after washing is removed to a beaker and a little sodium peroxide added which converts the alumina into sodium aluminate and is without action on the iron oxide. The beaker and contents should be allowed to stand for some hours, and the iron oxide then filtered off and weighed, the difference between this weight and the total oxides being alumina. It is important that the purity of the peroxide should be ascertained before use. A better method than the above is to place the weighed mixed oxides in a

porcelain or platinum boat in the combustion tube of a furnace and to ignite in a stream of hydrogen which reduces the ferric oxide, leaving the alumina unchanged. After reduction the boat is weighed again, and from the loss of weight the percentage of ferric oxide in the mixed precipitate can be calculated.

Estimation of Calcium.—The filtrate obtained above is heated until it boils, and 2 grms. of finely powdered ammonium oxalate is then slowly added, with constant stirring, the flame being removed meanwhile. The glass rod used for stirring is now rinsed into the beaker with distilled water, the contents of the beaker boiled for about two minutes, which causes the precipitate to become dense and more easy to filter. After standing for about half an hour the supernatant liquid is filtered through a Schleicher and Schüll No. 590 hard filter paper, the precipitate before transferring to the filter being washed as completely as possible by decantation. The precipitate is dried, ignited, and weighed either as carbonate or lime as already described for water.

Magnesium.—The filtrate from the lime precipitate is transferred to a conical flask fitted with a well-fitting rubber bung. Sodium phosphate is now added (Na_2HPO_4) and excess of ammonia, the contents of the flask thoroughly shaken for about twenty minutes and then allowed to stand over-night. The resulting precipitate of ammonium-magnesium phosphate is filtered off and washed with a mixture of 1 part of strong ammonia to 3 of water. The washed precipitate is dried, ignited, and weighed as pyrophosphate, the allowance being made as usual for the solubility of the precipitate in ammonia.

Sulphates.—These are determined in 50 c.c. of the original solution in the same manner as in water.

Available Lime.—Since the total calcium determined above will include both carbonates and oxides, a determination of combined carbon dioxide or available lime will be necessary. The latter may be readily obtained by weighing about 1 gm. of the powdered sample into a litre flask, which is then filled with distilled water (free from carbon dioxide) and well corked. The flask is occasionally shaken during the next few hours to ensure a complete solution of the lime. Now after allowing the undissolved sediment to settle, a portion of the solution is withdrawn by a pipette and titrated in a flask with decinormal acid and phenolphthalein. (Note that since phenolphthalein is very sensitive to carbon dioxide, titrations in which it is used are best carried out in small flasks.) Each cubic centimetre of acid used corresponds to .0028 gm. of lime, and if the total quantity thus found be deducted from that found by precipitation, the remainder may be assumed to be present in combination as calcium carbonate.

The above process may be considerably improved by substituting for water a solution of cane sugar, since lime dissolves very readily in this medium and a much larger sample may be taken. A 10 per cent.

solution of sugar may be employed, and instead of using 1 grm. of lime, as much as 10 grms. may be taken, and the filtrate finally titrated with fifth normal instead of decinormal soda.

Carbon dioxide may be determined directly by liberation with acid and expulsion from a weighed vessel, or volumetrically by collecting the evolved gas in a nitrometer, measuring and calculating the weight of the volume at 0° C. and 760 mm. pressure.

For the direct method Schrotter's apparatus is convenient. It is essentially a flask with three openings—that at A, fig. 14, closed by a glass stopper, is for the introduction of a weighed quantity of the substance; at B, a tap-funnel (also closed with a stopper) admits dilute sulphuric acid; C is a tube which allows the liberated CO₂ to escape after thorough drying by the strong sulphuric acid it contains. From 2 to 3 grms. of the lime are weighed into the flask of the apparatus, the tap-funnel is nearly filled with dilute, and the drying tube half filled with strong sulphuric acid. The stoppers, slightly greased, are inserted and the apparatus weighed. Acid from the funnel is then very slowly admitted

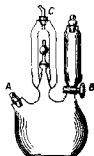


FIG. 14.

to the flask, so that the carbon dioxide escapes in single bubbles, passing through the strong sulphuric acid in the drying tube at a rate not faster than two per second. When effervescence has ceased the remaining dilute acid is run in, the tap opened, and the flask gradually heated until boiling just begins. At the same time the gaseous contents of the flask are aspirated by connecting the tube at the top of the drying apparatus with an aspirator by rubber tubing or simply sucking carefully with the mouth. Aspiration must not be unduly prolonged. When at an end the stopper is replaced in the tap-funnel, the apparatus allowed to cool and then weighed. To prevent the strong sulphuric acid in the drying tube from absorbing moisture from the air, it should be closed during weighing by a bit of rubber tubing plugged with glass rod. The loss of weight of the apparatus is the amount of carbon dioxide in the weight of lime taken.

In determining carbon dioxide volumetrically a small flask or bottle with a well-fitting rubber bung and delivery tube is connected with the two-way tap of a nitrometer by stout rubber tubing. Dilute acid is placed in the flask, and a short tube containing a weighed quantity of lime is carefully introduced so as not to bring the liquid into contact with the lime. The cork of the flask is tightly inserted, connection made with the nitrometer, and the reservoir so adjusted that with the mercury in the measuring tube up to the zero mark, pressure throughout the apparatus is atmospheric. The lime and acid in the flask are then mixed by gently rotating the flask, and the volume of the gas liberated and measured at the temperature and pressure of the atmosphere. The weight of each c.c. of carbon dioxide at 0° C. and 760 mm. is .00197 grm. This method, however, is of only approximate accuracy, it not being

possible to heat the lime and acid so as to insure complete decomposition of carbonates.

Chlorides may be tested for in the aqueous solution used in the determination of available lime. If present they are estimated by dissolving a weighed quantity of the lime in nitric acid, filtering and precipitating the filtrate with silver nitrate and weighing the resulting silver chloride. Since lime rarely contains much chloride, a fairly large sample should be taken for the estimation — not less than 5 grms. Having obtained a clear solution with nitric acid, a solution of silver nitrate is gradually added with constant stirring until no further precipitation occurs, which from the rapid subsidence and coagulation of the precipitate is readily observed. The liquid is then just raised to the boiling point, washed several times by decantation with hot distilled water, acidified with nitric acid, and filtered, well washed with hot water and dried. The precipitate may be collected either in a Gooch crucible on an asbestos mat or upon ordinary filter paper. The first is the quicker way, as, after well washing with hot water, the precipitate may be rinsed with alcohol and rapidly dried in the oven. If collected on a filter paper the dry precipitate must be removed from the paper, the paper ashed separately on the lid of a porcelain crucible, and any reduced silver reconverted into silver chloride by moistening successively with nitric and hydrochloric acid. The mass of the precipitate is heated in the porcelain crucible over a very small flame until it just begins to melt, when crucible and lid are cooled and weighed. The factor for converting silver chloride into chlorine is .2479.

Loss on ignition, which may be determined by igniting a small quantity in a platinum dish until constant in weight, will be due to moisture, carbon dioxide, and organic matter. If the carbon dioxide has been weighed or calculated as described above the water may be deduced by difference.

From the figures of the preceding determinations an accurate representation of the composition of the sample may be obtained.

Ammonia and its Salts.—Aqueous ammonia may be estimated accurately by means of its specific gravity if taken at a standard temperature with a delicate hydrometer. Table XII. gives the relation between specific gravity and strength.

Dilute solutions, if preferred, may be weighed in a stoppered bottle and titrated with standard acid and methyl orange or cochineal.

Ammonium Salts.—(a) *Direct Method.*—About .2–.5 gm. of the salt is weighed and dissolved in water and introduced into the flask of the apparatus (as in fig. 4). Excess of sodium hydrate solution, previously boiled to expel ammonia, is then added, and the ammonia is distilled into 50 c.c. of decinormal hydrochloric acid, the unused portion being afterwards titrated back with decinormal alkali and methyl-orange.

(b) *Indirect Method.*—About 1 gm. of the salt is accurately weighed and dissolved in water in a beaker or dish. Twenty-five c.c. of normal sodium

hydrate are then added and the solution boiled for twenty minutes to expel the ammonia. It is then cooled and the unused soda titrated back with normal acid, using methyl orange as indicator. Since 40 grms. of soda are required to expel 17 of ammonia, the quantity of ammonia present can easily be calculated.

TABLE XII.

Aqua Ammonia.

Be°.	Sp. gr.	% NH ₃ .	Be°.	Sp. gr.	% NH ₃ .	Be°.	Sp. gr.	% NH ₃ .
10.00	1.0000	0.00	16.50	0.9556	11.18	23.00	0.9150	23.52
10.25	0.9982	0.40	16.75	0.9540	11.64	23.25	0.9135	24.01
10.50	0.9964	0.80	17.00	0.9524	12.10	23.50	0.9121	24.50
10.75	0.9947	1.21	17.25	0.9508	12.56	23.75	0.9106	24.99
11.00	0.9929	1.62	17.50	0.9492	13.02	24.00	0.9091	25.48
11.25	0.9912	2.04	17.75	0.9475	13.49	24.25	0.9076	25.97
11.50	0.9894	2.46	18.00	0.9459	13.96	24.50	0.9061	26.46
11.75	0.9876	2.88	18.25	0.9444	14.43	24.75	0.9047	26.95
12.00	0.9859	3.30	18.50	0.9428	14.90	25.00	0.9032	27.44
12.25	0.9842	3.73	18.75	0.9412	15.37	25.25	0.9018	27.93
12.50	0.9825	4.16	19.00	0.9396	15.84	25.50	0.9003	28.42
12.75	0.9807	4.59	19.25	0.9380	16.32	25.75	0.8989	28.91
13.00	0.9790	5.02	19.50	0.9365	16.80	26.00	0.8974	29.40
13.25	0.9773	5.45	19.75	0.9349	17.28	26.25	0.8960	29.89
13.50	0.9756	5.88	20.00	0.9333	17.76	26.50	0.8946	30.38
13.75	0.9739	6.31	20.25	0.9318	18.24	26.75	0.8931	30.87
14.00	0.9722	6.74	20.50	0.9302	18.72	27.00	0.8917	31.36
14.25	0.9705	7.17	20.75	0.9287	19.20	27.25	0.8903	31.85
14.50	0.9689	7.61	21.00	0.9272	19.68	27.50	0.8889	32.34
14.75	0.9672	8.05	21.25	0.9256	20.16	27.75	0.8875	32.83
15.00	0.9655	8.49	21.50	0.9241	20.64	28.00	0.8861	33.32
15.25	0.9639	8.93	21.75	0.9226	21.12	28.25	0.8847	33.81
15.50	0.9622	9.38	22.00	0.9211	21.60	28.50	0.8833	34.30
15.75	0.9605	9.83	22.25	0.9195	22.08	28.75	0.8819	34.79
16.00	0.9589	10.28	22.50	0.9180	22.56	29.00	0.8805	35.28
16.25	0.9573	10.73	22.75	0.9165	23.04			

ALLOWANCE FOR TEMPERATURE.

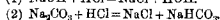
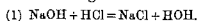
The coefficient of expansion for Ammonia Solutions varying with the temperature, correction must be applied according to the following table:—

Corrections to be added for each degree below 60° F.			Corrections to be subtracted for each degree above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14°	0.015° Bé	0.017° Bé	0.020° Bé	0.022° Bé	0.024° Bé	0.026° Bé
16	0.021 "	0.023 "	0.026 "	0.028 "	0.030 "	0.032 "
18	0.027 "	0.029 "	0.031 "	0.033 "	0.035 "	0.037 "
20	0.033 "	0.036 "	0.037 "	0.038 "	0.040 "	0.042 "
22	0.039 "	0.042 "	0.043 "	0.045 "	0.047 "	
26	0.053 "	0.057 "	0.057 "	0.059 "		

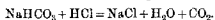
Alkalis.—The determination of impurities presents no difficulties. Iron, if present in traces, may be estimated colorimetrically by dissolving

in dilute acid and adding a little potassium ferrocyanide solution. Alumina, which is sometimes found in commercial caustic soda, is also separated from the hydrochloric acid solution by addition of ammonia and boiling. If much iron be present, the precipitate must be filtered off and washed into a clean beaker, treated with sodium peroxide and filtered, or the precipitate may be fused in a platinum capsule with sodium carbonate and a little potassium nitrate, and afterwards extracting the sodium aluminate with water and filtering off the unchanged iron oxide. If the solution of the aluminate be diluted and treated with ammonia, aluminium hydrate is precipitated, which is filtered off, ignited, and weighed. If sodium peroxide be used, the mixed hydrates of iron and alumina are boiled with a little of the compound, and filtered. The filtrate is then acidified with hydrochloric acid and boiled till all the hydrogen peroxide has been expelled, after which alumina is precipitated by ammonia.

Estimation of Sodium Carbonate and Hydrate.—A weighed quantity (about 10 grms.) is dissolved in distilled water, any insoluble matter being filtered off and weighed, and the filtrate collected in a 500 c.c. flask to which the washings are added, the whole being subsequently cooled and made up to 500 c.c. Fifty c.c. of this solution are now transferred to a conical flask, a few drops of phenolphthalein added and decinormal acid run in from a burette till the pink colour is just discharged. When this point is reached the whole of the hydrate and half of the carbonate will be neutralised, the remainder of the carbonate being transformed into bicarbonate.



After this any further addition of acid will decompose the bicarbonate, and the liberated carbon dioxide will discharge the colour of the phenolphthalein. A few drops of methyl orange are now added and the acid further run in till the yellow colour changes to a faint pink, when the whole of the carbonate will now be decomposed.



Evidently since, when the pink colour due to phenolphthalein was discharged, exactly half the carbonate had been decomposed, the total sodium present as carbonate must be equivalent to twice the quantity of acid required after the addition of the methyl orange, and therefore the sodium present as hydrate must be equivalent to the difference between the total acid used and that twice required to decompose the bi-carbonate. In working out the analysis the results are usually returned in terms of sodium oxide Na_2O .

The following is an actual example:

Wt. of soda ash taken = 10.024 grms.
made up to 500 c.c.

50 c.c. solution with phenolphthalein required 96 c.c. $\frac{N}{10}$ sulphuric acid.

After adding methyl orange the solution required 84 c.c. " "

Total acid. 180 c.c.

- ∴ Acid required by sodium carbonate :
- | | |
|---------------------|-------------|
| in 50 c.c. = 84 × 2 | = 168 c.c. |
| in 500 c.c. | = 1680 c.c. |
- ∴ $\text{Na}_2\text{CO}_3 = 1680 \times .0053$ grms. in 10.024 grms. = 88.8 or 51.9% Na_2O .
- Acid required by sodium hydrate :
- | | |
|-----------------------------|------------|
| in 50 c.c. = 180 - 168 c.c. | = 12 c.c. |
| in 500 c.c. | = 120 c.c. |
- ∴ Sodium hydrate = 120 × .004 = 4.8% = 3.61% Na_2O .

Arsenic sulphide is sometimes used for dehairing. The valuation of this body may be carried out by oxidising it to arsenic acid and precipitating as magnesium ammonium arsenate, which is subsequently converted into pyroarsenate by ignition and weighed. The method is as follows:—About 0.5 gm. of the finely powdered sample is weighed out into a beaker and boiled with strong nitric acid, covering the beaker with a clock glass. When solution is complete most of the acid is evaporated off on the water-bath and the residue diluted and filtered. To the clear filtrate excess of ammonia is added and magnesia mixture. After standing a day or more the precipitate is filtered off and washed with dilute ammonia. The precipitate is dried and the paper ashed apart from it in a porcelain crucible, to which the precipitate is then added, and the whole gradually raised to a red heat, which is maintained for 10 minutes. The ammonia will then have been expelled, and the residue of magnesium pyroarsenate $\text{Mg}_2\text{As}_2\text{O}_7$ can be weighed. To convert $\text{Mg}_2\text{As}_2\text{O}_7$ into As_2S_3 multiply by .7935; into As_2S_2 multiply by .6903.

Sodium Sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$).—Since sulphuretted hydrogen does not affect methyl orange, sodium sulphide may be titrated by means of decinormal acid in the presence of this indicator. From 10 to 12 grms. are weighed and dissolved in water, thus making approximately a decinormal solution. Fifty cubic centimetres of the solution are then withdrawn and titrated with methyl orange and decinormal acid. Each c.c. of acid used corresponds to .012 gm. of crystallised sodium sulphide or to .0023 gm. sodium.

The sulphur present as sulphide may be estimated by titration with a standard solution of zinc sulphate, using lead acetate paper as an indicator. A standard zinc solution is made by dissolving 287.55 grms. of pure recrystallised zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in water and adding ammonia till the precipitate is redissolved, when the solution is made up to a litre. Each c.c. of this solution corresponds to .03207 gm. sulphur.

" " .07817 " sodium sulphide.

Fifty c.c. of the sodium sulphide solution are placed in a beaker and the zinc solution added from a burette with frequent stirring until a drop of the liquid withdrawn by means of a pointed glass rod no longer gives any coloration with a piece of lead acetate paper placed by the side of the beaker. It is best to do the titration first of all rather quickly, to find out approximately the volume of zinc solution required, and then repeat the experiment, adding a little less than the volume found in the first titration

and then adding the zinc drop by drop, testing after each drop. This method is rapid and sufficiently accurate for most purposes, but more exact results may be obtained by oxidising the sulphide with sodium peroxide, precipitating the sulphate so obtained as barium sulphate, and weighing.

Oxidation by means of Sodium Peroxide.—Fifty c.c. of the solution are placed in a beaker and about 1 gm. of sodium peroxide added to the liquid, which is then gradually raised to the boiling point and maintained in gentle ebullition for about ten minutes. The liquid is acidified with dilute hydrochloric acid, boiled and precipitated with barium chloride solution, the resulting barium sulphate being filtered off, dried, and weighed. The weight of the sulphur in the precipitate is found by multiplying by the factor 0.13734.

Titration with Iodine.—The following alternative method of analysing sodium sulphide is due to F. Jean (*Analyst*, vol. xxii., p. 306). Ten grms. are dissolved in water, the deposited iron sulphide being determined in the insoluble matter. The filtrate is made up to a litre and 10 c.c. are titrated with decinormal iodine and starch solution to determine the total sulphur present. A second 10 c.c. mixed with 30 c.c. of water and a quantity of ammonium sulphate solution (6.7 grms. per litre strength), equal to the volume of the iodine solution used in the first test, are distilled, the retort being connected with the upper end of a vertical condenser, the lower end of which dips into 2 c.c. of decinormal acid. The distillation is continued till the distillate ceases to be alkaline. After boiling to expel sulphuretted hydrogen the excess of acid in the receiver is titrated with decinormal alkali and litmus. Each cubic centimetre of the acid neutralised by the distilled ammonia corresponds to 0.0039 gm. of sodium sulphide. The residue in the retort is cooled and titrated with decinormal iodine solution. Each cubic centimetre used is equivalent to 0.0079 gm. of sodium thiosulphate. The difference between this and the former iodine titration is calculated as sodium sulphide. By deducting from this the amount determined in the acid titration, a difference is obtained which represents in terms of sodium sulphide (Na_2S) the excess of sulphur present as polysulphide and may be calculated to sulphur ($100 \text{Na}_2\text{S} = 41\text{S}$). When the ammonium sulphide is pure the iodine and ammonia tests should give identical results. The following examples are given:—

	Green Sulphide.	Yellow Sulphide.
Water,	63.24	60.32
Sodium Sulphide,	31.20	28.00
Sulphur in Excess,	0.53	1.20
Sodium Thiosulphate,	4.70	10.00
Iron Sulphide,	0.33	0.46

Sodium sulphide sometimes contains very distinct traces of iron, and, if so, should be rejected.

Gas lime is still sometimes used for unhairing, but is largely replaced by artificially prepared sulphides or sulphhydrates of calcium. The total available lime and combined sulphur may be determined as described under sodium sulphides.

Analysis of spent Lime Liquors.—This is a matter of some importance to the tanner, as he is thereby enabled to check the loss of hide substance that is taking place, while a microscopic examination will reveal the presence of organisms that tend to destroy the hide substance. The following determination should be made:—

- | | | |
|---------------------|---|--------------------|
| (1) Total Solids. | } | (4) Caustic Lime. |
| (2) Organic Matter. | | (5) Combined Lime. |
| (3) Ammonia. | | (6) Sulphides. |

Total Solids.—It is of importance that lime liquors should be in contact with air as little as possible before being filtered, otherwise any calcium carbonate so formed will be arrested by the filter paper and hence the low results of the lime determined in the filtrate.

The liquor is best filtered through a large funnel having ground edges, to which is fitted a bell cap carrying a soda lime tube (fig. 15). By this means the CO_2 of the air is not in contact with the liquid before passing through the filter paper.

Fifty c.c. of the filtrate are collected, transferred to a platinum dish and treated with ammonium carbonate to convert the lime into carbonate. The liquid is then evaporated to dryness on the water-bath and dried in an air oven at 105° to 140° C. till constant in weight. The total solids so obtained are not the true total solids, exceeding them by the amount of carbon dioxide absorbed by caustic lime in the liquor. This being subsequently determined, its equivalent in carbon dioxide for 50 c.c. must be subtracted from the total solids. Instead of adding ammonium carbonate solution, carbonic acid gas may be bubbled into the liquor before evaporating.

Organic Matter.—The total solids are ignited until a white ash is obtained; the dish is then cooled and a little ammonium carbonate solution added and again dried on the water-bath to re-convert the lime into carbonate. When dry, the dish is very gently heated over a bunsen flame and again weighed. The loss in weight gives the total organic matter present. This organic matter includes, among other bodies, dissolved hide substance and peptones. The former should always be determined. For this purpose 50 c.c. of the filtered liquor are placed in a round-bottomed Jena glass

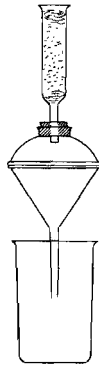


FIG. 15.

flask of about 300 c.c. capacity and gently boiled on a sand-bath until only occupying a volume of a few cubic centimetres. Ten c.c. of pure sulphuric acid are now added, together with a fragment of copper foil, and the flask again heated and the nitrogen subsequently determined by Kjeldahl's process. Since dried hide fibre contains 17.8 per cent. of nitrogen, the quantity of dissolved hide substance present in the liquid can easily be calculated, for every 17.8 parts of nitrogen found correspond to 100 parts of hide substance, or 1 part of nitrogen to 5.62 parts of hide substance.

Eitner determines organic substances as follows:—The lime in a measured volume of the filtered lime liquor is precipitated by bubbling in carbon dioxide, then boiling to complete precipitation and expel excess of the gas. The precipitate is collected on a weighed filter and washed. The lime is removed with dilute hydrochloric acid and the undissolved residue washed again with water, dried, and weighed. Eitner regards this as the organic matter (dissolved hide substance) combined with lime. On acidifying the filtrate with hydrochloric acid a further precipitate is obtained, which, when washed, dried and weighed, constitutes the organic substance uncombined with lime. Procter considers this distinction doubtful, it being unlikely that all organic compounds of lime would be decomposed by carbon dioxide.

Peptones are determined in the filtrate either by precipitation with sodium hypochlorite or with mercuric nitrate. In the latter, Hallopeau's method, described by Procter,¹ the neutral or slightly acid filtrate is mixed with its own volume of mercuric nitrate solution, allowed to stand for a day, and the precipitate then collected on a tared filter, washed with cold water until free from mercury, dried and weighed, and two-thirds of its weight taken as peptones. To prepare the mercuric nitrate solution, heat 150 grms. of commercial pure mercuric nitrate with 1 litre of water for 20 minutes, filter, heat nearly to boiling, and add sodium carbonate solution, drop by drop, with constant stirring until a permanent precipitate is produced, when the solution is again filtered for use.

Another method, probably preferable to the above, is that of Trotman and Hackford as applied in the analysis of glue. The hot filtered lime liquor is acidified and saturated with zinc sulphate which precipitates the albumose. The peptones in the filtrate are then precipitated with tannic acid, the compound of peptone and tannic acid filtered off, dried, and its content of nitrogen determined by Kjeldahl's method. The factor for conversion of nitrogen into peptones is 5.42.

Ammonia.—A suitable volume of the filtered liquor is placed in a conical flask fitted with a Kjeldahl delivery tube (fig. 16). The delivery tube dips into a measured volume of decinormal sulphuric acid in a flask. The flask is boiled for 15–20 minutes with a naked flame, a fragment of pumice stone being added to prevent frothing, at the end of which time a

¹ *Leather Industries Laboratory Book*, p. 82.

drop of methyl orange is added to the contents of the flask and the excess of acid titrated with decinormal alkali. Thus if 50 c.c. of acid were originally placed in the beaker and 13 c.c. of decinormal soda are required after the distillation, it is evident that the ammonia has neutralised 50 - 13 c.c., *i.e.* 37 c.c. of the acid, and hence the quantity liberated was $37 \times .0017$ gram.

A simpler though slower method is to place 25 c.c. of the lime liquor in a flat-bottomed glass dish standing on a ground-glass plate (fig. 17). Next rest a glass triangle on the top of the dish, upon it stand a dish containing 25 c.c. of decinormal sulphuric acid, and enclose the whole under a bell-jar of which the greased rim grips the ground-glass plate. After a couple of days the ammonia will have left the lower dish and combined with the acid in the upper one. The excess of combined acid is then titrated with methyl orange and standard soda solution.

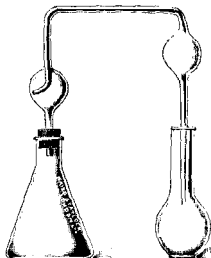


FIG. 16.

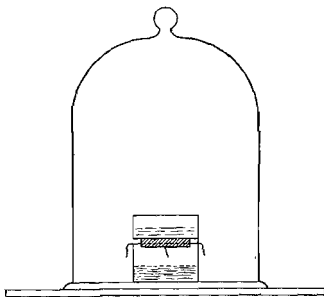


FIG. 17.

Procter and McCandlish (*J.S.C.I.*, 1906, 254) have described a new method and apparatus for estimating ammonia in lime liquors. Pure air is drawn through the ammoniacal liquor into standard acid (fig. 18).

A tube A ($\frac{3}{16}$ in. in diam.), drawn out to a fine point, is bent as shown, and another tube B widened at the end is fitted over it, the two being held in position by wiring to a cork fixed between them. Over the end of B is placed the head of a thistle-funnel sealed at the point where the stem

enters the head, and the whole is introduced into a large test-tube (10 in. by 2 in.), and containing enough water to cover the junction of A and B, the tubes being so adjusted that a continuous stream of water is carried through the tube B with the air, some of the air escaping from the bottom of B and passing outside it. The tubes are then fastened in the tube and broken glass is packed nearly up to the level of the thistle funnel. The test tube is closed by a two-holed rubber bung, admitting pure air from the coupled U-tubes into A and the passage of ammonia-laden air into the U-tube containing standard acid. This device both prevents frothing and secures the complete distribution and aeration of the lime liquor. The

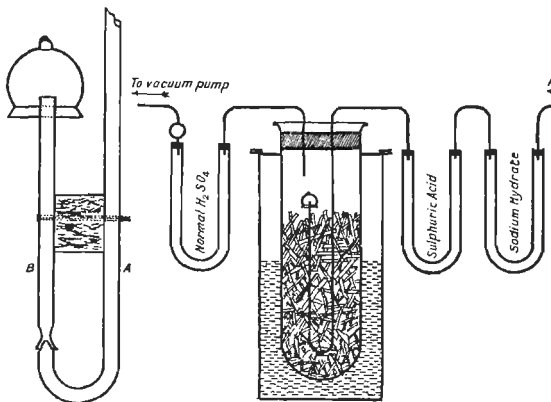


FIG. 18.

U-tube containing the standard acid is connected with the water-pump by a tube with a bulb which serves to arrest splashes of acid.

To bring the lime liquor into the test-tube, tube A is disconnected from the coupled U-tubes and the liquor poured into it through a funnel with the help of gentle suction from the water-pump. The filled tube is immersed in a water-bath heated to 90°C ., which keeps the lime liquor at about 65°C . Under these conditions all the ammonia may be removed from 50 c.c. of lime liquor in about half an hour.

Caustic Lims.—This may be estimated either in the same volume of liquid from which the ammonia has been expelled by one of the preceding methods or in another portion of the lime liquor from which the ammonia has been rapidly driven off by boiling in an open flask or beaker. If the third method of ammonia estimation has been employed, a fresh portion

had better be taken for the determination of caustic lime. To the ammonia-free liquid a few drops of phenolphthalein solution are added and decinormal acid run in with constant stirring until the pink colour just disappears. Each c.c. of acid corresponds to .0028 grm. of lime. If soda be also present it will be included with the lime. It should be tested for in the ignited total solids by heating with carbonate of ammonia and extracting with distilled water, filtering, and washing the filter thoroughly. Since calcium carbonate is practically insoluble in water, an alkaline filtrate will denote the presence of soda, and the amount may be measured by titrating with methyl orange and standard acid. It must, however, be remembered that barium carbonate is fairly soluble in water, and hence its absence in the above filtrate must be proved before calculating to sodium. If barium be present, a white precipitate will be obtained with decinormal sulphuric acid.

Combined Lime.—Fifty c.c. of the liquor are evaporated in a platinum dish and ignited and reconverted into carbonates by means of ammonium carbonate, as in the determination of total solids. The residue is dissolved in hydrochloric acid and filtered and the lime precipitated by means of ammonium oxalate.

In the absence of soda or after its removal, if present, by washing as described above, the residue may be simply dissolved in an excess of standard acid, and after gently boiling for a minute the unused acid titrated with methyl orange and decinormal alkali. From the total lime thus found is deducted that present as caustic lime. The difference is the amount of lime combined with organic acids.

Sulphides are determined in the original liquor by one of the methods described above.

After the completion of the chemical analysis, cover-slip microscope slides stained with carbol-fuchsin should be made. A fresh lime liquor contains but a few bacteria, but an old or used one will show a large number, and it may be stated that, as a general rule, liquors showing a large number of bacteria are unsuitable for depilating purposes. To make the preparation, spread a little of the liquid on a thin cover-slip and dry by gently warming, finally passing the slip twice through the flame. Then float it in a warm solution of carbol fuchsin or other dye for a minute, after which the excess of dye is washed away with distilled water and the slip mounted wet in glycerine or gently dried and mounted with canada balsam.

CHAPTER VII.

DELIMING.

A DESCRIPTION of the various methods now in use for deliming will be found in Procter's *Principles of Leather Manufacture*. As many of the bodies used for deliming have also curing and other properties, it will be convenient to include some of them in this chapter. The following are the general methods of analysis of the deliming agents more commonly used:—

(1) **Mineral Acids** (sulphuric and hydrochloric).—The approximate strength of the acids may be found from their specific gravities, provided, of course, that no mineral bodies are present. The specific gravity may be taken by means of a glass hydrometer at 15° C., or more accurately by a pycnometer specific gravity bottle, as shown in fig. 19. An ordinary bottle should not be used, since sulphuric acid rapidly attracts moisture from the air and hydrochloric acid loses strength unless enclosed in a stoppered bottle. Having taken the specific gravity, the percentage of real acid may be deduced from Tables XIV.—XVI. (Ferguson, *J.S.C.I.*, 1905, 781).

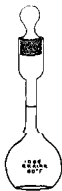


FIG. 19.

A more exact measurement may be carried out by accurately weighing a small quantity of the acid in a stoppered weighing bottle, or graduated flask, diluting to a known volume and titrating an aliquot part with standard alkali, using methyl orange as an indicator.

(2) **Organic Acids**.—Lactic, acetic, formic, and oxalic acid may all be estimated by titrating a weighed quantity with standard alkali and phenolphthalein. Methyl orange is not a good indicator for organic acids. In titrating with phenolphthalein as indicated, it is best to run alkali from a burette till a faint pink colour is obtained. The following are the factors for use with decinormal soda:—

TABLE XIII.

1 c.c. decinormal soda equals	0·006	grm. acetic acid.
	0·009	„ lactic „
	0·0046	„ formic „
	0·0045	„ oxalic „

Oxalic acid may be titrated with methyl orange if a little neutral calcium chloride is added.

TABLE XIV.
Nitric Acid.

Be.	Sp. gr.	Tw.	HNO ₃	Be.	Sp. gr.	Tw.	HNO ₃	Be.	Sp. gr.	Tw.	HNO ₃
10.00	1.0741	14.82	12.86	23.60	1.1855	37.70	30.40	36.00	1.3303	66.06	52.30
10.25	1.0761	15.22	13.18	23.25	1.1910	38.25	30.36	36.25	1.3334	66.68	52.81
10.50	1.0781	15.62	13.40	22.50	1.1934	38.68	31.21	36.50	1.3364	67.28	53.32
10.75	1.0801	16.02	13.81	22.75	1.1959	39.18	31.58	36.75	1.3395	67.90	53.84
11.00	1.0821	16.42	14.13	24.00	1.1983	39.66	31.94	37.00	1.3426	68.52	54.36
11.25	1.0841	16.82	14.44	24.25	1.2008	40.16	32.31	37.25	1.3457	69.14	54.89
11.50	1.0861	17.22	14.76	24.50	1.2033	40.66	32.68	37.50	1.3488	69.76	55.43
11.75	1.0881	17.62	15.07	24.75	1.2058	41.16	33.05	37.75	1.3520	70.40	55.97
12.00	1.0902	18.04	15.41	25.00	1.2083	41.66	33.42	38.00	1.3551	71.02	56.52
12.25	1.0922	18.44	15.72	25.25	1.2109	42.18	33.80	38.25	1.3583	71.66	57.08
12.50	1.0943	18.86	16.05	25.50	1.2134	42.83	34.17	38.50	1.3615	72.30	57.65
12.75	1.0964	19.28	16.39	25.75	1.2161	43.20	34.56	38.75	1.3647	72.94	58.23
13.00	1.0985	19.70	16.72	26.00	1.2185	43.70	34.94	39.00	1.3679	73.58	58.82
13.25	1.1006	20.12	17.05	26.25	1.2211	44.22	35.33	39.25	1.3712	74.24	59.43
13.50	1.1027	20.54	17.38	26.50	1.2230	44.72	35.70	39.50	1.3744	74.88	60.06
13.75	1.1048	20.96	17.71	26.75	1.2262	45.24	36.09	39.75	1.3777	75.54	60.71
14.00	1.1069	21.38	18.04	27.00	1.2288	45.76	36.48	40.00	1.3810	76.20	61.38
14.25	1.1090	21.80	18.37	27.25	1.2314	46.28	36.87	40.25	1.3843	76.86	62.07
14.50	1.1111	22.22	18.70	27.50	1.2340	46.80	37.26	40.50	1.3876	77.52	62.77
14.75	1.1132	22.64	19.02	27.75	1.2367	47.34	37.67	40.75	1.3909	78.18	63.48
15.00	1.1154	23.06	19.36	28.00	1.2393	47.86	38.06	41.00	1.3942	78.84	64.20
15.25	1.1176	23.52	19.70	28.25	1.2420	48.40	38.46	41.25	1.3976	79.52	64.93
15.50	1.1197	23.94	20.02	28.50	1.2446	48.92	38.85	41.50	1.4010	80.20	65.67
15.75	1.1219	24.38	20.36	28.75	1.2472	49.40	39.25	41.75	1.4044	80.88	66.42
16.00	1.1240	24.80	20.69	29.00	1.2500	50.00	39.60	42.00	1.4078	81.56	67.18
16.25	1.1262	25.24	21.03	29.25	1.2527	50.54	40.06	42.25	1.4112	82.24	67.95
16.50	1.1284	25.68	21.36	29.50	1.2554	51.08	40.47	42.50	1.4146	82.92	68.73
16.75	1.1306	26.12	21.70	29.75	1.2582	51.64	40.89	42.75	1.4181	83.62	69.52
17.00	1.1328	26.56	22.04	30.00	1.2609	52.18	41.30	43.00	1.4216	84.32	70.33
17.25	1.1350	27.00	22.38	30.25	1.2637	52.74	41.72	43.25	1.4251	85.02	71.15
17.50	1.1373	27.46	22.74	30.50	1.2664	53.28	42.14	43.50	1.4286	85.72	71.98
17.75	1.1395	27.90	23.08	30.75	1.2692	53.84	42.58	43.75	1.4321	86.42	72.82
18.00	1.1417	28.34	23.42	31.00	1.2719	54.38	43.00	44.00	1.4356	87.12	73.67
18.25	1.1440	28.80	23.77	31.25	1.2747	54.94	43.44	44.25	1.4392	87.84	74.53
18.50	1.1462	29.24	24.11	31.50	1.2775	55.50	43.89	44.50	1.4428	88.56	75.40
18.75	1.1485	29.70	24.47	31.75	1.2804	56.08	44.34	44.75	1.4464	89.28	76.28
19.00	1.1508	30.16	24.82	32.00	1.2832	56.64	44.78	45.00	1.4500	90.00	77.17
19.25	1.1531	30.62	25.18	32.25	1.2861	57.22	45.24	45.25	1.4536	90.72	78.07
19.50	1.1554	31.08	25.55	32.50	1.2889	57.78	45.68	45.50	1.4573	91.44	79.03
19.75	1.1577	31.54	25.88	32.75	1.2918	58.36	46.14	45.75	1.4610	92.20	80.04
20.00	1.1600	32.00	26.24	33.00	1.2946	58.92	46.58	46.00	1.4646	92.92	81.08
20.25	1.1624	32.48	26.61	33.25	1.2975	59.50	47.04	46.25	1.4684	93.68	82.18
20.50	1.1647	32.94	26.96	33.50	1.3004	60.08	47.49	46.50	1.4721	94.42	83.33
20.75	1.1671	33.42	27.33	33.75	1.3034	60.68	47.95	46.75	1.4758	95.16	84.48
21.00	1.1694	33.88	27.67	34.00	1.3063	61.26	48.42	47.00	1.4796	95.92	85.70
21.25	1.1718	34.36	28.02	34.25	1.3093	61.86	48.90	47.25	1.4834	96.68	86.98
21.50	1.1741	34.82	28.36	34.50	1.3122	62.44	49.35	47.50	1.4872	97.44	88.32
21.75	1.1765	35.30	28.72	34.75	1.3152	63.04	49.83	47.75	1.4910	98.20	89.76
22.00	1.1789	35.78	29.07	35.00	1.3182	63.64	50.32	48.00	1.4948	98.96	91.26
22.25	1.1813	36.29	29.43	35.25	1.3212	64.24	50.81	48.25	1.4987	99.74	93.13
22.50	1.1837	36.74	29.78	35.50	1.3242	64.84	51.30	48.50	1.5026	100.52	95.11
22.75	1.1861	37.22	30.14	35.75	1.3273	65.46	51.80				

ALLOWANCE FOR TEMPERATURE:

- At 10°-20° Be. = 1.30° Ba. or 0.00029 Sp. Gr. = 1° F.
- 20°-30° Be. = 1.23° Ba. or 0.00044 " " = 1° F.
- 30°-40° Be. = 1.20° Ba. or 0.00060 " " = 1° F.
- 40°-48.5° Be. = 1.17° Ba. or 0.00084 " " = 1° F.

The purity of an organic acid should of course be established by qualitative tests. A great many commercial acids contain distinct traces of iron which is in many ways objectionable. This should be tested for by means of potassium ferrocyanide or sulphocyanate, and if the quantity present be small, estimated by colorimetric methods. Sulphuric acid

should also be tested for the presence of nitric acid; if present the acid will become brown on the addition of ferrous sulphate solution owing to the formation of nitric oxide.

TABLE XV.

Hydrochloric Acid.

Be.	Sp. gr.	Tw.	HCl.	Be.	Sp. gr.	Tw.	HCl.	Be.	Sp. gr.	Tw.	HCl.
1.99	1.0660	1.28	1.40	16.0	1.1240	24.80	24.57	20.8	1.1675	33.50	32.95
2.00	1.0140	2.80	3.82	16.1	1.1243	24.90	24.73	21.0	1.1684	33.68	33.12
3.00	1.0211	4.22	4.25	16.2	1.1256	25.12	24.90	21.0	1.1694	33.88	33.21
4.00	1.0284	5.68	5.69	16.3	1.1265	25.30	25.06	21.1	1.1703	34.06	33.60
5.00	1.0367	7.14	7.15	16.4	1.1274	25.48	25.23	21.2	1.1713	34.26	33.69
5.25	1.0375	7.80	7.82	16.5	1.1283	25.66	25.39	21.3	1.1722	34.44	33.99
5.50	1.0384	7.88	7.89	16.6	1.1292	25.84	25.56	21.4	1.1732	34.64	34.07
5.75	1.0413	8.26	8.26	16.7	1.1301	26.02	25.72	21.5	1.1741	34.84	34.26
6.00	1.0422	8.64	8.64	16.8	1.1310	26.20	25.89	21.6	1.1751	35.02	34.45
6.25	1.0450	9.00	9.02	16.9	1.1310	26.38	26.05	21.7	1.1760	35.20	34.64
6.50	1.0469	9.38	9.40	17.0	1.1325	26.56	26.22	21.8	1.1770	35.40	34.83
6.75	1.0488	9.76	9.78	17.1	1.1336	26.72	26.39	21.9	1.1779	35.58	35.02
7.00	1.0507	10.14	10.17	17.2	1.1345	26.90	26.56	22.0	1.1789	35.78	35.21
7.25	1.0526	10.52	10.55	17.3	1.1354	27.08	26.73	22.1	1.1798	35.96	35.40
7.50	1.0545	10.90	10.94	17.4	1.1363	27.26	26.90	22.2	1.1808	36.16	35.59
7.75	1.0564	11.28	11.32	17.5	1.1372	27.44	27.07	22.3	1.1817	36.34	35.78
8.00	1.0584	11.68	11.71	17.6	1.1381	27.62	27.24	22.4	1.1827	36.54	35.97
8.25	1.0603	12.06	12.09	17.7	1.1390	27.80	27.41	22.5	1.1836	36.72	36.16
8.50	1.0623	12.46	12.48	17.8	1.1399	27.98	27.58	22.6	1.1846	36.92	36.35
8.75	1.0642	12.84	12.87	17.9	1.1408	28.16	27.75	22.7	1.1856	37.12	36.54
9.00	1.0662	13.24	13.26	18.0	1.1417	28.34	27.92	22.8	1.1866	37.32	36.73
9.25	1.0681	13.62	13.66	18.1	1.1426	28.52	28.09	22.9	1.1875	37.50	36.92
9.50	1.0701	14.02	14.04	18.2	1.1435	28.70	28.26	23.0	1.1885	37.70	37.14
9.75	1.0721	14.42	14.43	18.3	1.1444	28.88	28.44	23.1	1.1895	37.90	37.36
10.00	1.0741	14.82	14.83	18.4	1.1453	29.06	28.61	23.2	1.1904	38.08	37.56
10.25	1.0761	15.22	15.22	18.5	1.1462	29.24	28.78	23.3	1.1914	38.28	37.80
10.50	1.0781	15.62	15.62	18.6	1.1471	29.42	28.95	23.4	1.1924	38.48	38.03
10.75	1.0801	16.02	16.01	18.7	1.1480	29.60	29.13	23.5	1.1934	38.68	38.26
11.00	1.0821	16.42	16.41	18.8	1.1489	29.78	29.30	23.6	1.1944	38.88	38.49
11.25	1.0841	16.82	16.81	18.9	1.1498	29.96	29.48	23.7	1.1953	39.06	38.72
11.50	1.0861	17.22	17.21	19.0	1.1508	30.16	29.65	23.8	1.1963	39.26	38.95
11.75	1.0881	17.62	17.61	19.1	1.1517	30.34	29.83	23.9	1.1973	39.46	39.18
12.00	1.0902	18.04	18.01	19.2	1.1526	30.52	30.00	24.0	1.1983	39.66	39.41
12.25	1.0922	18.44	18.41	19.3	1.1535	30.70	30.18	24.1	1.1993	39.86	39.64
12.50	1.0943	18.80	18.82	19.4	1.1544	30.88	30.35	24.2	1.2003	40.06	39.86
12.75	1.0964	19.28	19.22	19.5	1.1554	31.06	30.53	24.3	1.2013	40.26	40.06
13.00	1.0985	19.70	19.63	19.6	1.1563	31.26	30.71	24.4	1.2023	40.46	40.32
13.25	1.1006	20.12	20.04	19.7	1.1571	31.44	30.89	24.5	1.2033	40.66	40.55
13.50	1.1027	20.54	20.45	19.8	1.1581	31.62	31.08	24.6	1.2043	40.86	40.78
13.75	1.1048	20.96	20.86	19.9	1.1590	31.80	31.27	24.7	1.2053	41.06	41.01
14.00	1.1069	21.38	21.27	20.0	1.1600	32.00	31.45	24.8	1.2063	41.26	41.24
14.25	1.1090	21.80	21.68	20.1	1.1609	32.18	31.64	24.9	1.2073	41.46	41.48
14.50	1.1111	22.22	22.09	20.2	1.1619	32.38	31.82	25.0	1.2083	41.66	41.72
14.75	1.1132	22.64	22.50	20.3	1.1628	32.56	32.01	25.1	1.2093	41.86	41.99
15.00	1.1154	23.06	22.92	20.4	1.1637	32.74	32.19	25.2	1.2103	42.06	42.30
15.25	1.1176	23.52	23.33	20.5	1.1647	32.94	32.38	25.3	1.2114	42.26	42.64
15.50	1.1197	23.94	23.75	20.6	1.1656	33.12	32.56	25.4	1.2124	42.46	43.01
15.75	1.1219	24.38	24.16	20.7	1.1666	33.32	32.75	25.5	1.2134	42.68	43.40

ALLOWANCE FOR TEMPERATURE :

10°-15° Be. -- 1/40° Be. or 0.0002 Sp. Gr. for 1° F.

15°-22° Be. -- 1/20° Be. or 0.0003 " " 1° F.

22°-25° Be. -- 1/25° Be. or 0.00035 " " 1° F.

Formic Acid.—*Determination of Formic Acid by Potassium Permanganate*¹ consists in oxidising formic acid in a boiling alkaline solution by means of an excess of potassium permanganate, then adding an excess of oxalic, and finally titrating the excess of oxalic with permanganate.

¹ J. Klein, *Ber.*, 1906, vol. xxxix., p. 2640.

DELMING.

TABLE XVI.
Sulphuric Acid.

Be°.	Sp. gr.	Tw.	Per cent. H ₂ SO ₄	Weight of 1 cu. ft. in lbs. Av.	Per cent. O. V.	Pounds 1 cu. ft.	Freezing Point (Melting Point).	APPROXIMATE BOILING POINTS.						
								50° Be, 295° F.	60° " 386° "	61° " 400° "	62° " 415° "			
0	1.0000	0.0	0.00	62.37	0.00	0.00	32.0° F.							
1	1.0069	1.4	1.02	62.80	1.09	0.68	31.2 "							
2	1.0140	2.8	2.08	63.24	2.23	1.41	30.5 "							
3	1.0211	4.2	3.13	63.69	3.36	2.14	29.8 "							
4	1.0284	5.7	4.21	64.14	4.52	3.30	28.9 "							
5	1.0357	7.1	5.28	64.60	5.67	3.66	28.1 "							
6	1.0432	8.6	6.37	65.06	6.84	4.45	27.2 "							
7	1.0507	10.1	7.45	65.53	7.99	5.24	26.3 "							
8	1.0584	11.7	8.55	66.04	9.11	6.06	25.1 "							
9	1.0662	13.2	9.66	66.50	10.37	6.89	24.0 "							
FIXED POINTS.														
10	1.0741	14.8	10.77	66.99	11.56	7.74	22.8 "							
11	1.0821	16.4	11.89	67.49	12.76	8.61	21.5 "							
12	1.0902	18.0	13.01	68.00	13.96	9.49	20.0 "	1.0000	0.00	1.6281		62.34		
13	1.0985	19.7	14.13	68.51	15.16	10.39	18.3 "	1.0048	0.71	1.6440		63.79		
14	1.1069	21.4	15.25	69.04	16.36	11.30	16.6 "	1.0347	5.14	1.6748		65.61		
15	1.1154	23.1	16.38	69.57	17.58	12.23	14.7 "	1.0649	9.48	1.6272		71.00		
16	1.1240	24.8	17.53	70.10	18.81	13.19	13.6 "	1.0992	14.22	1.6679		74.48		
17	1.1328	26.6	18.71	70.65	20.03	14.13	10.2 "	1.1353	19.04	1.7044		77.54		
18	1.1417	28.3	19.89	71.21	21.24	15.20	7.7 "	1.1736	25.94	1.7358		79.40		
19	1.1508	30.2	21.07	71.78	22.61	16.23	4.8 "	1.2105	28.55	1.7472		81.32		
20	1.1599	32.0	22.25	72.35	23.87	17.27	+ 1.6 "	1.2513	33.49	1.7700		83.47		
21	1.1694	33.9	23.44	72.94	25.14	18.34	- 1.8 "	1.2951	38.54	1.7959		86.36		
22	1.1789	35.8	24.61	73.53	26.41	19.42	- 0.0 "	1.3441	44.15	1.8117		88.63		
23	1.1885	37.7	25.81	74.13	27.69	20.53	- 1.1 "	1.3947	49.52	1.8194		89.75		
24	1.1983	39.7	27.03	74.74	29.00	21.68	- 1.6 "	1.4307	53.17	1.8275		91.82		
25	1.2083	41.7	28.28	75.36	30.34	22.87	- 2.3 "	1.4667	56.58	1.8354		93.19		
26	1.2185	43.7	29.53	76.00	31.69	24.08	- 3.0 "	1.4822	58.14					
27	1.2288	45.8	30.79	76.64	33.04	25.32	- 3.9 "							
28	1.2393	47.9	32.05	77.30	34.39	26.58	- 4.9 "							
29	1.2500	50.0	33.33	77.96	35.76	27.88	- 6.1 "							
30	1.2609	52.2	34.63	78.64	37.16	29.22	- 7.4 "							
31	1.2719	54.4	35.93	79.33	38.55	30.58	- 8.2 "							
32	1.2832	56.6	37.26	80.03	39.98	32.00	- 9.6 "							
33	1.2946	58.9	38.58	80.74	41.40	33.42	- 9.7 "							
34	1.3063	61.2	39.92	81.47	42.83	34.90	- 9.1 "							
35	1.3182	63.6	41.27	82.22	44.28	36.41	- 8.1 "							
36	1.3303	66.1	42.63	82.97	45.74	37.95	- 7.0 "							
37	1.3426	68.5	43.99	83.74	47.20	39.53	- 6.0 "							
38	1.3551	71.0	45.35	84.52	48.66	41.13	- 5.2 "							
39	1.3679	73.6	46.72	85.32	50.13	42.77	- 4.7 "							
40	1.3810	76.2	48.10	86.13	51.61	44.45	- 4.1 "	61.93	53.34	77.36		66.63		
41	1.3942	78.8	49.47	86.96	53.08	46.16	- 3.5 "	63.60	55.30	79.58		69.19		
42	1.4078	81.5	50.87	87.80	54.58	47.92	- 3.1 "	65.50	57.50	81.81		71.83		
43	1.4216	84.3	52.26	88.67	56.07	49.72	- 2.7 "	67.28	59.86	84.05		74.53		
44	1.4356	87.1	53.66	89.54	57.58	51.58	- 2.3 "	69.09	61.86	86.30		77.27		
45	1.4500	90.0	55.07	90.44	59.09	53.44	- 2.0 "		70.90	88.56		80.10		
46	1.4646	92.9	56.48	91.35	60.60	55.26	- 1.4 "		72.72	90.43		82.98		
47	1.4796	95.9	57.90	92.28	62.13	57.33	- 1.5 "		74.55	93.79		85.92		
48	1.4948	98.9	59.32	93.23	63.65	59.34	- 1.8 "		76.37	97.40		88.94		
49	1.5104	102.1	60.75	94.20	65.18	61.40	- 2.2 "		78.22	73.08		92.03		
50	1.5263	105.3	62.18	95.20	66.72	63.52	- 2.7 "	80.06	76.21	100.00		95.20		
51	1.5426	108.5	63.66	96.21	68.31	65.72	- 3.3 "	81.96	78.85	102.38		98.50		
52	1.5591	111.9	65.13	97.24	69.89	67.96	- 3.9 "	83.96	81.54	104.74		101.85		
53	1.5761	115.2	66.63	98.30	71.50	70.28	- 4.9 "	85.79	84.33	107.15		105.38		
54	1.5934	118.7	68.13	99.38	73.11	72.66	- 5.0 "	87.72	87.17	109.57		108.89		
55	1.6111	122.2	69.65	100.48	74.74	75.10	..	89.67	90.10	112.01		112.55		
56	1.6292	125.6	71.17	101.61	76.37	77.99	..	91.63	93.11	114.46		115.20		
57	1.6477	129.5	72.75	102.77	78.07	80.23	..	93.87	94.26	117.00		120.24		
58	1.6667	133.3	74.36	103.95	79.79	82.95	..	95.74	99.52	119.69		124.31		
59	1.6860	137.2	75.99	105.16	81.54	85.75	- 7 "	97.84	102.89	122.21		128.63		

TABLE XVI.—*continued.**Sulphuric Acid.*

Be.	Sp. gr.	Tw.	Per cent H ₂ SO ₄	Weight of 1 cu. ft. in lbs. Av.	Per cent. O. V.	Pounds O. V. in 1 cu. ft.	Freezing (Melting) Point.	Per cent. 60°	Pounds 60° in 1 cu. ft.	Per cent. 50°	Pounds 50° in 1 cu. ft.
60	1.7059	141.2	77.67	106.40	85.35	88.98	+12.0° F.	100.00	106.40	124.91	132.91
61	1.7262	146.2	79.43	107.66	85.23	91.76	27.3 "	102.27	110.10	127.74	137.52
62	1.7470	149.4	81.39	108.96	87.24	95.06	39.1 "	104.67	114.05	130.75	142.47
63	1.7683	153.7	83.34	110.29	89.43	98.03	48.1 "	107.30	118.94	134.03	147.22
64	1.7901	158.0	85.06	111.95	91.92	102.03	46.4 "	110.29	123.14	137.76	153.81
64½	1.7957	159.1	86.33	112.90	92.64	103.75	43.6 "	111.15	124.40	138.84	155.50
64¾	1.8012	160.2	87.04	112.34	93.49	104.93	41.1 "	112.06	125.89	139.98	157.26
65	1.8068	161.3	87.81	112.69	94.23	106.19	37.9 "	113.05	127.40	141.22	159.14
65½	1.8125	162.5	88.65	113.05	95.13	107.54	33.1 "	114.14	129.03	142.57	161.17
66	1.8182	163.6	89.55	113.44	96.10	108.97	24.6 "	115.30	130.75	144.02	163.82
66½	1.8230	164.8	90.60	113.76	97.22	110.60	13.4 "	116.65	132.70	145.71	165.76
66¾	1.8297	166.9	91.80	114.12	98.51	112.42	- 1 "	118.19	134.88	147.68	168.48
66	1.8354	167.1	93.19	114.47	100.00	114.47	- 29 "	119.98	137.34	149.87	171.56

	H ₂ SO ₄	O. V.	60°
O. V.	93.19	100.00	119.98
60°	77.67	89.35	100.00
50°	82.13	66.72	80.06

Acids stronger than 66° Be should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, *Journal of Chemical Society*, vol. lvii, p. 308.

*Formic Acid and its Salts. Gasometric Valuation.*¹—Two c.c. of a 10 per cent. solution of the salt to be examined are placed in the Flask I, shown in the illustration. The tube of the tap funnel is previously filled

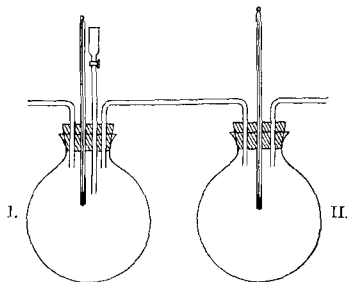


FIG. 20.

with water up to the tap, whilst the bulb of the funnel contains about 30 c.c. of concentrated H₂SO₄. Flask II. acts as a drying flask, 40 c.c. of strong H₂SO₄ being placed within it. The second flask is connected to the nitrometer containing KOH solution. After removing all the air from the

¹ M. Wegner, *Zeits. anal. Chem.*, 1903, xlii. [6 and 7], 427-431, and *J.S.C.I.*, 1903, 1619.

apparatus by means of a current of carbon dioxide, the acid in the second flask being at the same time heated to 180°, the acid in the funnel is allowed to run on to the formate in I. At the end of this reaction the flask is also warmed to 180° C. and CO₂ again passed to carry all the CO into the mitrometer. The formic acid is not completely decomposed in the first flask, and any moisture collecting in the tube between the flasks must be driven over by the aid of a small flame. Traces of formic acid which escape with the moisture in the first flask are decomposed in the second.

The percentage of sodium formate is found from the volume of CO by the formula

$$x = \frac{v(\beta - W) \times 0.1251 \times 68}{760(1 + 0.00367t) \times s \times 28}$$

in which

v = volume of CO.

W = vapour pressure of KOH
in mm. at t° C.

68 = M.W. of sodium formate.

s = wt. of substance taken.

β = barometer reading.

t = temperature centigrade.

0.001251 gm. = wt. of 1 c.c. CO.

28 = M.W. of CO.

Acetic and volatile inorganic acids do not interfere with the method, but oxalic, if present, must be removed by precipitation. If tartaric, citric, malic or similar acids be present, they must be separated from the formic by distillation. Should the sodium formate contain sodium nitrite, the nitrous acid may be destroyed by adding ammonium chloride and boiling under a reflux condenser for an hour.

Separation and Estimation of Formic and Acetic Acids.—Both acids combine with yellow mercuric oxide, but whilst mercuric formate is reduced on boiling to metallic mercury the acetate is unchanged and may be separated by filtration. The experiments may be conducted as follows:—

(1) Determine total acid by titration.

(2) Boil a measured volume of the acid with excess of yellow mercuric oxide, and filter.

(3) If acetic acid be present the filtrate will contain mercuric acetate, and the addition of H₂S will precipitate mercuric sulphide. Filter off, dry and weigh on a filter paper previously dried and weighed at 100° C. From the weight of mercuric sulphide calculate the equivalent of acetic acid.

(4) If formic acid be present, the residual mercuric oxide will contain metallic mercury. Transfer the mixture to a beaker, dissolve the excess of mercuric oxide in dilute hydrochloric acid and filter off the remaining mercury. Wash, dry at 100° C. and weigh, from the weight calculating the equivalent of formic acid. Acetic and formic acid may also be separated by neutralising with excess of calcined magnesia or lead carbonate, filtering off the salts produced and concentrating to a small bulk, after which excess of alcohol is added. Formate of magnesia or lead is precipitated while the acetates remain in solution.

Special Method for Determination of Lactic Acid.—Lactic acid is not very much adulterated and its determination is very difficult on account of

the solubility of all its salts. If other acids have been proved to be absent it can be estimated by direct titration; in the presence of other acid the total acid must be determined and the percentage of foreign acids, the difference being lactic acid.

The presence of anhydride in commercial lactic acid renders the determination of the latter by direct titration untrustworthy. The following method is proposed by Philip.¹ About 5 grms. or 5 c.c. of the sample are diluted with water and titrated with $\frac{N}{1}$ NaOH, using phenolphthalein as indicator. A measured excess of alkali solution is then added, the mixture boiled, and the excess of alkali titrated back. The first titration gives the amount of actual lactic acid, and the quantity of alkali used in the second corresponds to the amount of anhydride present. One c.c. $\frac{N}{1}$ alkali = 0.09 gm. lactic acid and 0.162 gm. of the anhydride. Corrections should be made for sulphuric acid if it be present.

Boric Acid.—This acid should not be directly titrated with caustic alkali, except in the presence of glycerine or mannite. If, however, the solution contains at least 30 per cent. glycerine it may be titrated with caustic soda, using phenolphthalein as indicator. The neutral point corresponds to the formation of NaBO_2 . Each c.c. of decinormal alkali is equivalent to .0062 of crystallised boric acid.

In making the determination the following points should be observed. Solid borax or boric acid may be carefully neutralised with hydrochloric acid and methyl orange, then boiled for a minute to expel carbonic acid, cooled, mixed with a third of its volume of glycerine and titrated. The glycerine, which often contains carbonic acid, should before use be made neutral to phenolphthalein.

Solutions containing boric acid should be made alkaline with soda and concentrated, then neutralised and boiled as above. The presence of organic matter necessitates evaporation to dryness and incineration, while if phosphates be present the procedure must be modified as follows:—The ash is dissolved in hydrochloric acid and about .5 gm. of calcium chloride and a few drops of phenolphthalein are added, and normal soda until the mixture is pink. Twenty-five c.c. of lime water is now added and the mixture made up to 100 c.c. An aliquot portion is filtered, normal acid added until the pink colour just fades, when the solution is made first acid and then just alkaline to methyl orange. The estimation is continued as already described.

In the presence of other acids boric, like lactic, acid must be estimated by deduction, or it may be converted into methyl borate, and estimated directly as its lime salt. The experiment is performed as follows:—First make the acid alkaline with soda, and evaporate to dryness, and, if organic matter be present, incinerate. Next transfer the ash by means of methyl alcohol and a few drops of water to a conical flask with a rubber

stopper through which passes a tap funnel and delivery tube. The flask is attached to a condenser, and sufficient acetic acid is added through the funnel to make the contents distinctly acid. Then about 5 c.c. of methyl alcohol is introduced, and the liquor distilled nearly to dryness in an oil-bath, the distillate being collected in a vessel containing a known quantity of lime. After the first distillation a further quantity of 5 c.c. of methyl alcohol is added, and the distillation repeated until the residue in the flask gives no reaction for boric acid with turmeric paper. The vessel containing the lime and distillate is now dried and ignited until of constant weight. The increase in weight is due to boric acid. The process is improved by using sodium phosphate instead of lime. Twenty c.c. of approximately 2 per cent. solution is added to the collected distillate, and the whole evaporated to dryness and weighed. At the same time a similar quantity of the phosphate solution is evaporated and ignited in a second dish. The difference in weight between the two residues is due to boric acid. Instead of weighing, the distillate may be collected in excess of caustic soda solution which is then concentrated to a small bulk, exactly neutralised with mineral acid and methyl orange, then boiled to expel carbonic acid, after which 30 per cent. of glycerine is added, and the boric acid titrated as above.

Carbolic Acid.—The analysis of carbolic acid may be conducted on the following lines:—

Determination of Phenols and Neutral Oils.—Ten c.c. of the sample are placed in a graduated tube or burette, and about four times its volume of a 10 per cent. solution of sodium hydroxide (free from alumina) is gradually added. The tube is now corked and well shaken, when the acids will dissolve, leaving the neutral oils, which will, on standing, form a layer at the top or bottom of the tube. The volume of this layer may be read off. The reading may be made easier by adding a measured quantity of petroleum, shaking and reading again, deducting the volume of petrol added. This layer of neutral oils may now be removed by means of a separating funnel, the aqueous layer returned to the graduated tube and acidified, when the phenols will be liberated. These are read off in the same way as neutral oils.

Determination of Moisture.—A measured quantity is distilled from a retort or distilling flask, the distillate being collected in a graduated cylinder in which the aqueous layer is measured.

The above process for assaying carbolic acids is not always applicable, and, in general, more accurate results are obtained by the following method, which may be used for complex disinfecting or curing liquids containing tar acids:—

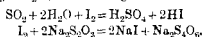
One hundred c.c. of the sample are distilled from a 4-oz. retort by means of a naked flame, the distillation being continued till charring takes place or a temperature of 300°–325° C. is reached. The distillate is warmed and shaken in a separating funnel with about 30 c.c. of 20 per cent. sodium hydrate solution. The lower alkaline layer containing the tar acids is

drawn off and the residue shaken again with a small quantity of the alkaline solution. The residue, after extraction with alkali, will consist of neutral oils, which are run into a graduated cylinder and measured. The alkaline solution of tar acids is then transferred to a graduated cylinder and acidified with sulphuric acid and allowed to cool. The liberated tar acids will form a layer on the surface which may be read off.

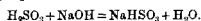
Many complex disinfecting liquids contain resin and other soaps. These may be treated with sulphuric acid and the layer which separates collected and distilled. A still better method is to distil with superheated steam at a temperature of from 200° to 220° C., at which temperature phenolates are readily decomposed to the exclusion of the soap. The distillate is treated in the manner described above.

Sulphurous Acid.—Two methods are applicable to the analysis of liquors containing sulphurous acid.

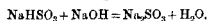
Titration with Iodine.—A weighed quantity of the material is introduced into a stoppered bottle, acidified, and an excess of decinormal iodine solution added in order to oxidise the sulphurous to sulphuric acid. After allowing to stand for a few minutes dilute with distilled water, and add decinormal sodium thiosulphate from a burette till the colour has almost disappeared. Then add a few drops of a solution of soluble starch in water, and continue the addition of the thiosulphate, shaking after each drop, until the blue colour has just disappeared. From the number of cubic centimetres of thiosulphate used we find the quantity of unused iodine, and by difference the number of c.c. of decinormal iodine solution used in oxidising sulphurous to sulphuric acid. Each c.c. of decinormal iodine is equal to 0.032 gm. of sulphur dioxide, 0.126 gm. of crystallised sodium sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, or 0.045 gm. of metabisulphite.



Estimation of Free Sulphurous Acid in the Presence of Bisulphites.—Bisulphites are neutral to methyl orange and acid to phenolphthalein. This fact may be taken advantage of in the following way. To a measured quantity of the solution to be analysed add a little of each indicator and then decinormal caustic soda until the solution is neutral to methyl orange, when the free sulphurous acid will be present as bisulphite of soda, as shown by the following equation:—



Having read the volume of soda used, it is again added until a faint pink colour is produced, which denotes that the whole of the sulphurous acid present is converted into sodium sulphite in accordance with the equation



Each c.c. of alkaline used is equivalent to 0.032 of SO_2 , and from the first reading can be calculated the amount of free sulphurous acid, while the second reading will give the amount of sulphur dioxide present.

as bisulphite. If the amount of free sulphurous acid calculated from the first reading be deducted from that given by the second, the percentage of bisulphite originally present can be calculated.

A mixture of bisulphite and neutral sulphite can be analysed in a similar way. The acid sulphite is first titrated with caustic soda and phenolphthalein, and then the total neutral sulphite consisting of that originally present, and that which has been formed from the bisulphite, is titrated with methyl orange and decinormal hydrochloric acid.

Analysis of Drenches.—The analysis of a drench is usually confined to the determination of total and volatile acid. These may be determined by titrating a measured volume of the filtered liquid with decinormal soda and phenolphthalein, and then boiling a second similar portion to expel volatile acids and titrating again to determine fixed acid. The quantity of acid varies from 1 to 3 grms. per litre. If a more extended analysis is required the following method of Wood and Wilcox (*J.S.C.I.*, 1893, 422) may be used.

Volatile Bases.—Two or three litres of the drench are placed in a distillation flask with 5 grms. of pure chalk and distilled until the distillate is neutral and nearly odourless. The distillate is made acid with HCl and evaporated to a small bulk. The liquid containing the hydrochlorides of any volatile bases present in the drench may be tested—

- (1) For primary amines by the isonitrile reaction (warming with chloroform and alcoholic potash);
- (2) For alkaloids with phospho-molybdic acid.

If these be absent and the original distillate had a strong fishy odour, trimethylamine may be suspected. To confirm, prepare the platinum salt by evaporating down the concentrated solution of its hydrochloride with excess of platinum chloride, and if obtained in sufficient quantity determine the molecular weight of the base.

Volatile Acids.—To neutralise the 5 grms. of chalk originally placed in the flask 100 c.c. of normal hydrochloric acid would be required, when all the acids originally in the volume of drench taken would be liberated. By adding the HCl in portions the excess of CaCO_3 may first be neutralised and the various volatile acids to some extent separated by successive additions of normal HCl followed by distillation. Sufficient normal HCl should first be added until the distillate begins to come over faintly acid. Ten c.c. of normal HCl are then added and the mixture distilled until the distillate ceases to be acid. Three more fractions are distilled off in the same way, using 10, 10, and 20 c.c. of normal acid respectively. From the fractions so obtained the barium salts of the acids in solution are prepared by neutralising with barium carbonate, filtering and evaporating to dryness. These may be examined qualitatively for the acid by preparing their characteristic ethyl esters with alcohol and sulphuric acid. Wood and Wilcox found by this method formic, butyric, and acetic acids, but their estimation is difficult.

Non-volatile acids are tested for in another portion of the drench. Four litres are evaporated down to 1 litre and filtered. The clear liquid is again concentrated, filtered, and made up to 500 c.c. Lactic acid is the non-volatile acid most likely to be present, Wood and Wilcox testing for it as follows:—Ten c.c. of the liquid are placed in a small distillation flask, 2 c.c. of conc. sulphuric acid and .5 grm. potassium bichromat~~e~~ in a little water are added, and the mixture distilled, and the vapour condensed in a test-tube surrounded by cold water. Aldehyde in the distillate may be recognised by its smell, but to confirm, add magenta solution just decolorised with SO₂ solution. The restoration of the colour proves the presence of acetaldehyde in the distillate and of lactic acid in the liquid distilled. Wood and Wilcox found no other non-volatile acid; they determined the lactic acid both by direct titration of the filtered concentrated drench and by extracting the acid in the pure state, preparing and weighing its calcium salt.

Analysis of Bran.—The composition of bran is given by Wood and Wilcox as:—

TABLE XVII.

Water,	14 per cent.
Fibrin,	15 „
Starch,	44 „
Fat,	4 „
Lignose and Cellulose,	17 „
Ash,	6 „

The chief determinations in the valuation of a starch are moisture, mineral matter, and starch, while free acid may be determined where the sample shows any sign of fermentation.

Moisture and Ash are determined in the usual way. An excessively damp sample will generally be sour, while a high ash content would point to adulteration with mineral matter.

Starch may be determined in either of the following ways.¹ Five grms. of the finely powdered sample are extracted in a Soxhlet apparatus with alcohol of specific gravity 0.920 for several hours to remove reducing substances and soluble nitrogenous compounds. A little solid paraffin may be added to the extraction flask to prevent frothing. The extracted flour is well boiled with 100 c.c. of water and cooled to 57° C. Ten c.c. of a filtered cold water extract of ground malt are now added and the mixture kept at 57° C. for one hour, or until no further blue colour is given with iodine solution. The solution is then boiled, filtered into a 200 c.c. flask, the residue well washed and the volume made up after cooling. Twenty c.c. of the solution are now withdrawn and the cupric reducing power determined with Fehling solution, and the maltose calculated from the reduced copper. The starch can be calculated from the knowledge that 84.4 parts of maltose correspond to 100 parts of

¹ Brown and Millar, *Brewing Review*, 1904, xviii. 101.

starch. A correction should be made for the reducing power of the malt solution used.

Instead of using malt extract the residual flour may be boiled for six hours with 2 per cent. acid.

Determination of Fibre.—Five grms. of the powder is extracted with petroleum ether to remove the fat. This may be done either in a Soxhlet apparatus or by allowing it to stand over-night in a corked flask and decanting off the solution next morning. The residue is now allowed to boil gently for half an hour with 50 c.c. of 5 per cent. sulphuric acid and 75 c.c. of distilled water, adding water from time to time to replace that lost by evaporation. The beaker is then filled with cold water and allowed to stand until the insoluble matter has settled, the liquid being subsequently decanted through a piece of linen, leaving as much of the fibre in the beaker as possible. The solid matter on the linen is washed back into the beaker, 50 c.c. of 5 per cent. potash added, and 75 c.c. of water, and the liquid boiled again for half an hour as before. It is now filtered through linen again, and after washing clean the insoluble matter is removed by a wash-bottle to a platinum dish, dried and weighed, after which it is ashed. The first weight minus the ash gives the amount of fibre present.

Analysis of Dung.—This should include the determination of moisture, organic matter, and mineral matter. A further and more detailed analysis should include total soluble matter, nitrogen, phosphoric acid and mineral matter insoluble in water. The analysis may be conducted on the following lines:—

Moisture.—Five grms. of the sample are dried in a platinum dish till constant in weight.

Mineral Matter.—The dried residue is ashed at a low temperature, the loss in weight giving the total organic matter present and the residue the mineral matter.

Soluble Ash.—The ash is extracted with hot distilled water and filtered, the residue being thoroughly washed till quite neutral. The filtrate is now titrated with decinormal soda and methyl orange, the result being calculated to potash. The insoluble residue is washed back into a beaker, boiled with hydrochloric acid, filtered again, and the undissolved silica ignited and weighed.

Determination of Nitrogen.—Ten grms. of the substance are placed in a Kjeldahl flask and acidified with dilute acid and partly dried. Twenty-five c.c. of sulphuric acid are then added and the Kjeldahl analysis proceeded with in the ordinary way, except that when the solution is completed the liquid should be made up to 100 c.c. with distilled water and an aliquot portion withdrawn for determination of ammonia. It is necessary to take a somewhat large sample of the original substance in order to get a fair average.

Total Soluble Matter.—This may be determined by thoroughly shaking

a portion of the sample with distilled water, filtering through a 605 filter paper and evaporating a measured quantity of the filtrate to dryness. •

Lime and Phosphoric Acid.—If these determinations be made the following method should be employed:—

Determination of Lime.—A weighed quantity of the material is dried and ignited to destroy organic matter, the ash is weighed and 2 grms. placed in a beaker, 10 c.c. of dilute hydrochloric acid is added, the beaker covered with a clock glass and warmed on the water-bath until all effervescence due to carbonates has ceased; a further 20 c.c. of strong hydrochloric acid is then added and evaporated to dryness on the water-bath. When dry, well moisten the residue with 5 c.c. of hydrochloric acid and dry again on the water-bath, in order to render the silica insoluble. Then dissolve in about 20 c.c. of dilute acid and filter off the silica, which may be weighed if necessary. To the filtrate add ammonia until a precipitate is formed. Then add 2 grms. of powdered citric acid dissolved in a small quantity of water. If the precipitate dissolves add ammonia until it is again thrown down, and then sufficient strong acetic acid to re-dissolve it. If the precipitate does not dissolve, no further addition of ammonia is necessary, the precipitate being simply dissolved in acetic acid. The ammonium citrate thus formed prevents the precipitation of phosphates of iron and alumina, while the presence of acetic acid is necessary for the determination of lime. Now raise the liquid to the boiling point, add about 2 grms. of powdered ammonium oxalate little by little with constant stirring, and after boiling for 2 minutes allow the precipitated calcium oxalate to settle. Filter it off and wash thoroughly, ignite in a platinum crucible until no further loss of weight takes place—that is to say, until the whole of the oxalate is transformed into lime—and weigh.

Determination of Phosphoric Acid.—Concentrate the filtrate if necessary, until it does not measure more than 200 c.c.; add 50 c.c. of strong ammonia and 40 c.c. of magnesium chloride mixture, and, after stirring thoroughly, allow the mixture to stand for a couple of hours with frequent stirring, then decant the liquid through a filter paper, leaving as much of the precipitate as possible in the beaker. Next place the beaker containing the precipitate under the funnel and wash the filter paper with dilute hydrochloric acid, until the precipitate on the paper and that in the beaker are dissolved. Now wash the paper once with dilute ammonia (1:3), and add sufficient strong ammonia to the beaker to allow of this being about a quarter of the whole volume. Let it stand for about one hour with frequent stirring. Decant off the liquid and wash the precipitate as far as possible by decantation, using a mixture of one volume of strong ammonia to three of water, and continuing the washings until a drop of the filtrate made acid with nitric acid gives no cloudiness with silver nitrate. The precipitate is now dried, ignited in a platinum crucible and weighed as magnesium pyrophosphate $Mg_2P_2O_7$, the weight of the precipitate multi-

plied by '64 giving the weight of phosphoric acid. The phosphoric acid may be converted into tricalcic phosphate $\text{Ca}_3\text{P}_2\text{O}_8$ by multiplying by the factor 2.1831.

The above method is not quite accurate, since magnesium-ammonium phosphate is distinctly soluble in water, slightly soluble in a mixture of ammonia and water, and more so in the presence of ammonium salts and citrates. It is found that if the precipitation be conducted as described above, the results obtained are about 0.33 per cent. too low. If these directions have been followed, 0.33 may be added to the percentage of phosphoric acid obtained.

The Composition of Dung.—Insufficient is known of the composition to fix rigid standards, but Wood (*J.S.C.I.*, 1894, p. 220) gives the following figures. This substance lends itself so easily to adulteration that it would always repay systematic analysis.

TABLE XVIII.

(1) <i>Hen Dung.</i> —	
Water,	60.88
Organic matter,	19.22 cont. 6.24 ammonia.
Phosphates,	4.47
Calcium carbonate and sulphate,	7.85
Alkaline salts,	1.09
Silica, etc.,	6.40
(2) <i>Dog Dung.</i> —	
Water,	31.0
Organic matter,	14.2
Mineral matter, ¹	54.8

An adulterated sample gave water, 89.0; mineral matter, 1.5; organic matter, 9.5.

¹ Including alkaline salts, 0.8; phosphoric acid, 3.4.

Procter (*Principles of Leather Manufacture*) gives the following results of two analyses of pigeon dung:—

TABLE XIX.

	Min.	Max.	Mean.
Water,	3.80	40.00	21.00
Nitrogen,	1.47	5.04	2.53
Phosphoric acid,	1.00	2.77	1.79
Potash,	1.71	2.57	1.46

CHAPTER VIII.

THE QUALITATIVE RECOGNITION OF DIFFERENT TANNINS.

Owing to the complex nature of the tannins and the difficulty of isolating and recognising their disintegration products, there is up to the present time no scientific method of qualitatively recognising them, and we have only certain empirical colour reactions to rely on. These, though in some cases fairly satisfactory when dealing with a pure extract, are of comparatively little value in the case of mixtures. The following description of these tests, together with the tables of reactions, are due to Procter¹ (*J.S.C.I.*, 1894, p. 487, and *L.I.L.B.*, p. 68). The strength of the tannin solutions used should be approximately 0.5 per cent.

Reaction with Ferric Alum in 1 per cent. Solution.—With this reagent catechol tannins give a greenish-black coloration or precipitate. Pyrogallol and certain other tannins give blue-black colorations. Thus a tannin giving a greenish-black colour is certain to be a catechol derivative, but a good many which are undoubtedly catechol tannins together with some pyrogallol tannins give bluish-black, so that the production of this colour is not decisive.

Bromine Water, when added to a solution of a catechol tannin, produces a precipitate, while pyrogallol tannins give none. Some of the tannins giving the blue-black with iron produce a precipitate with bromine, but these are generally believed to be catechol derivatives.

Cupric Sulphate and Ammonia.—When a solution of cupric sulphate is added to a tannin solution followed by a little ammonia, a precipitate is produced consisting of a mixture of tannate of copper and cupric hydroxide. If excess of ammonia be added the precipitate dissolves, in many cases forming a greenish-brown or purplish-brown solution, but in the case of gallotannic acid and many tannins containing protocatechuic an insoluble tannate of copper remains. Very dilute solutions of copper should be used, or the blue solution formed by the addition of excess of ammonia will disguise the coloration due to the tannin. These three reactions enable us to broadly subdivide the tannins. Thus we have—

¹ By permission of the author.

Class 1.—Catechol tannins, which give a precipitate with bromine and green black with iron alum. These can be further subdivided as follows:—

(a) Copper salt soluble in excess of ammonia. See Table XXII.

(b) Copper salt insoluble in ammonia. See Table XXIII.

Class 2.—Tannins giving a precipitate with bromine and bluish colour with iron alum.

Class 3.—Tannins which give no precipitate with bromine and bluish colour with iron.

Classes 2 and 3 may be to a certain extent subdivided by means of nitrous acid.

Nitrous Acid Reaction (Procter).—A little dilute tannin infusion is placed in a porcelain dish and an excess of a freshly prepared solution of sodium or potassium nitrite is added, followed by three to five drops of decinormal sulphuric acid. In typical cases the solution instantly turns pink or crimson and slowly changes through purple to indigo-blue, but in other cases the final colour is green or brownish. According to Procter, *Classes 2 and 3* may, by means of this reaction, be further divided into two sub-classes, according to whether or not a colour reaction is obtained with nitrous acid. Thus—

Class 2.—No reaction with nitrous acid (Table XXIV.).

Positive reaction with nitrous acid (Table XXV.).

Class 3.—No reaction with nitrous acid (Table XXVII.).

Positive reaction with nitrous acid (Table XXVI.).

Having thus divided the tannins into certain broad groups, certain other colour reactions may be noted, viz.:

Stannous Chloride. Hydrochloric Acid.—To 10 c.c. of a strong solution of stannous chloride in hydrochloric acid are added 1 c.c. of the tannin infusion in a porcelain dish, and allowed to stand for 10 minutes. Certain tans, such as conifers, mimosa, and larch, give pink colorations.

Phloroglucol Reaction.—A fragment of deal is soaked in the infusion and dried, and then moistened with hydrochloric acid and gently dried. Certain materials, which probably contain phloroglucol, give a bright red or violet colour.

Sodium Sulphite.—A crystal of sodium sulphite is added to a few drops of the infusion in a dish. Many tannins, particularly valonia, give a pink coloration.

Concentrated Sulphuric Acid.—A test-tube is rinsed out with the infusion and drained, so that only a few drops remain. One cubic centimetre of strong sulphuric acid is then poured carefully down the side of the sloped tube so as to form a layer beneath the tannin solution. A large number of tanning materials give a crimson coloration at the junction of the liquids, while others give brownish yellow, etc. The colour having

been noted, the layers are mixed and diluted with water and the colour of the dilute solution observed.

Lime Water.—This is added in excess to an infusion of the tannin. Parker and Payne recommend mixing the liquor with a considerable excess of $\frac{N}{5}$ lime water, made by dissolving lime in sugar and water, the experiment being carried out in a stoppered cylinder.

Thus mangrove gives a deep red; mimosa, lavender colour; myrobalans, a brown yellow; and sumach, if pure, gives a bright canary yellow, changing to a brilliant green, but if it be adulterated with any quantity of either pistacia or tamarix, the colour produced is a deep brown; no trace of green colour appears on standing.

Diazobenzene Chloride.—According to Nierenstein (*J.S.C.I.*, 1906, 912) all pyrocatechol tannins, such as quebracho, give a precipitate when a .5 per cent. solution of the reagent is added to a cold extract of the tannin; the reaction is not given by pyrogallol tannins.

Investigation of an Unknown Tannin.—In the present state of knowledge as to the chemistry of the tannins, practically all that can be done towards the investigation of an unknown natural tannin is to determine whether it belongs to the catechol or pyrogallol groups, since all known tannins are derived from one of these compounds, and when carefully distilled in a retort, yield either one or both of these bodies. Catechin and gallic acid yield catechol and pyrogallol also when distilled, but they may be removed from the accompanying tannins by dissolving them in water and shaking the solution with ether. Further information may also be obtained by studying the products of decomposition by acids or fusion with caustic alkali. Catechol tannins also sometimes yield phloroglucol, an isomer of pyrogallol. These bodies may be recognised by their reactions with the following reagents:—

- (1) Ferric alum.
- (2) Lime water.
- (3) Deal shavings and hydrochloric acid.
- (4) Bromine water.

TABLE XX.

	Pyrogallol.	Catechol.	Phloroglucol.
Ferric alum, . . .	Blue-black, turning green and brown.	Dark green.	No reaction.
Lime water, . . .	Violet coloration, turning rapidly brown.	No marked reaction.	„
Bromine water, . . .	No colour.	„ „	Whitish precipitation.
Deal shavings and hydrochloric acid, . . .	„	„	Violet-red colour.

PROCTER'S TABLES.

TABLE XXI.

PRELIMINARY CLASSIFICATION OF TANNING MATERIALS.

CLASS 1. (CATECHOL TANNINS.)

Br. Water produces a Precipitate.
Iron-Alum gives Greenish Blacks.

Copper Sulphate followed by Ammonia in Excess.

Precipitate redissolves. 1 α TABLE XXII.	Precipitate does not redissolve. 1 β TABLE XXIII.
---	---

CLASS 2. (MIXED AND DOUBTFUL.)

Br. Water produces a Precipitate.
Iron-Alum gives Blue or Purplish Blacks.

Sodium Nitrite and 5 drops $\frac{N}{10}$ HCl.

(Nitrous Acid Reaction.)

No reaction, or, at most, darkening. 2 α TABLE XXIV.	Some Colour-Change through Red towards Blue or Green. 2 β TABLE XXV.
---	---

CLASS 3. (PYROGALLOL TANNINS.)

Br. Water produces no Precipitate.
Iron-Alum gives Blue Blacks.

Sodium Nitrite and 5 drops $\frac{N}{10}$ HCl.

Colour-Change through Red to Blue. 3 α TABLE XXVI.	No reaction. 3 β TABLE XXVII.
---	---

TABLE XXII.—continued.

Class i. a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SnCl ₃ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.
Garrulle (front bark of <i>Kermes oak</i>) (<i>Quercus coccifera</i>).	Green-black coloration.	Pp.	Reacts?	Pp. redissolves brown.	No reaction.	No reaction.	Reddens.	Crimson, dilutes pink.	Reddish brown pp.
Quercitron bark (<i>Quercus tinctoria</i>).	Do.	Pp.	Reacts somewhat.	Do.	Light green.	Do.	Doubtful.	Do.	Do.
Gambier (ext. of leaves of <i>Nasella gambier</i>).	Deep green coloration.	Pp.	No reaction, darkens.	Pp. redissolves olive-green.	Yellow.	Deep violet-red.	Yellow.	Crimson, dilutes brown.	No pp.
4 " Prun bast" (leaves of <i>Colpomen</i> or <i>Oxyris compressa</i>).	Green-black.	Pp.	No reaction.	Pp. redissolves greenish.	No reaction.	Pink.	Do.	Do.	Light yellow pp.
3 " Koko" (leaves of <i>Colostera buxifolia</i>).	Do.	Pp.	Do.	Do.	Do.	No reaction.	Do.	Dark brown.	Bright yellow pp.
Larch bark (<i>Larix sibirica</i>).	Green-black coloration.	Pp.	No reaction, darkens.	Pp. redissolves olive-green.	Pink coloration.	Do.	No reaction, darkens.	Deep red-brown.	Rusty pp.
Hemlock bark (<i>Tsuga</i> or <i>Abies canadensis</i>).	Olive-green reddish pp.	Pp.	No reaction, pink with NaNO ₂ .	Pp. redissolves neutral tint.	Do.	Do.	Reddens.	Crimson, dilutes pinkish.	Red-brown pp.
"Larch" extract from <i>Abies cecilia</i> .	Green-black or brown.	Pp.	No reaction.	Pp. redissolves olive-green.	Do.	Do.	Darkens.	Deep red-brown.	Brown pp.

1 Dyes yellow with Al and Sn mordants.

2 Used at Cape of Good Hope as sumach.

3 Used in Natal as sumach anilinoide.

 4 *Fichte, Rothbäume, Norway* or common spruce. 5 *Abies pectinata*, the *Wiese- or Egel-Tanne* or silver fir, is said to give a blue-black with iron.

TABLE XXIII.

Class I B.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₄	H ₂ SO ₄	Lime Water
Willow-bark (Russian. Sp. unknown).	Green-black.	Fp.	No reaction.	Dense pp.	No reaction.	Violet faint.	Pink coloration.	Red-brown, not intense.	Slight greyish pp.
<i>Acacia Anglica</i> or <i>Piptadenia macrocarpa</i> bark.	Do.	Fp.	Do.	Dense chocolate pp.	Pink or violet colour.	Do.	Reddens somewhat.	Crimson, dilutes pink.	Reddish pp.
<i>Acacia catenata</i> bark.	Do.	Fp.	Do.	Dense violet-black pp.	Possible trace.	Trace.	Pink colour.	Red-brown.	Flesh colour
"Thorn tree" bark (<i>Acacia horrida</i>), Cape.	Do.	Fp.	No reaction, darkens.	Dense pp.	No reaction.	Doubtful.	Do.	Dull crimson, not intense.	No pp.
Mangrove bark extract (<i>Rhizophora mangle</i>).	Do.	Fp.	No reaction.	Reddish-black.	Slight reddening.	No reaction	Slight reddening.	Red-brown.	Red pp., darkened by excess.
Quebracho wood extract (<i>Quercus</i> or <i>Lacosterygium</i> , Venezuela).	Green-black coloration	Fp.	Do.	Dense pp.	Pink colour pp.	Trace.	Doubtful.	Crimson coloration, dilutes pink.	Light-brown pp.
"Sugar-bush" bark (Cape) (<i>Protea mellifera</i>).	Green-black.	Fp.	No reaction, darkens.	Do.	No reaction.	Do.	Do.	Red.	Yellow-brown pp.
"Wagenboom" (Cape) (<i>Protea grandiflora</i>).	Do.	Fp.	Do.	Do.	Do.	Do.	Pink colour.	Crimson, dilutes pink.	Light yellow pp.
"Kruppelboom" (Cape) (<i>Leucospermum comocarpum</i>).	Do.	Fp.	Do.	Do.	Do.	Violet distinct.	Do.	Do.	Slight greyish pp.
"Silver tree" (Cape) (<i>Leucodendron argentea</i>).	Do.	Fp.	Do.	Do.	Do.	No reaction.	Pink coloration.	Do.	Flesh colour pp.
1 Chestnut Oak (<i>Quercus prinus</i>).	Olive-green coloration.	Fp.	Reacts distinctly.	Decided pp. Insoluble in excess.	Do.	Do.	Reddens.	Crimson, dilutes pinkish.	Reddish-brown pp.

1 Infusions fluoresce, especially with ammonia.

TABLE XXIV.

Class 2 a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SuCl ₂ + HCl.	Deal Shaving and HCl.	N ₂ O ₅ SO ₃ .	H ₂ SO ₄ .	Lime Water.
"Skens," <i>Cyperus Sumbach</i> (<i>Fistacia tescus</i>). ¹ Kliphaat bark ² (<i>Rhus Thunbergii</i>).	Blue-black. pp. Blue-black.	Pp. Pp.	No reaction. Do.	Dark pp. Dense dark pp.	No reaction. Do.	No reaction. Do.	Yellow. Pink.	Yellow-brown. Dull crimson, dilutes orange.	Yellow pp., darkening. Pinkish pp.
<i>Cousigne</i> (Root of <i>Rumex hymenosepalus</i>).	Blue-black pp.	Pp.	Do.	Do.	No reaction, clouds.	Trace violet.	Slight darkening.	Yellow-brown.	Pink coloration, greyish pp. Reddish-brown pp.
"Talwan" or "Elands-bontjes" (Root <i>Elaeagnus serrata</i> <i>Burkhardtii</i>).	Do.	Pp.	No reaction, darkens.	Do.	No reaction.	Do.	Pink.	Red.	
Mimosa or Wattle barks (various Austral. <i>Acacia</i>).	Dirty violet pp.	Pp.	No reaction.	Dense purple-brown pp. Dense dark pp.	Slight reddening.	Sometimes trace.	Reddens.	Crimson, dilutes pink.	Reddish or yellow-brown pp.
Babool bark, India (<i>Acacia arabica</i>).	Do.	Pp.	Do.	Do.	Some trace.	Faint trace.	Slight darkening.	Crimson, dilutes orange.	Dark reddish-brown pp.
Dark red Austr. bark (probably an <i>Acacia</i>).	Do.	Pp. needle crystals.	Do.	Deep violet pp.	No reaction.	Do.	Orange pink.	Crimson, dilutes pink.	Bright violet pp.
"White bark" <i>Agerodes blanda</i> , South America (a <i>Prosepe</i> or <i>Acacia</i>).	Do.	Pp.	Do.	Reddish-black pp.	Do.	Violet.	Reddens strongly.	Do.	Red pp., turning violet.

¹ Also known as "schink" or "stineo," and used to adulterate Sicilian annuach.

² Used at Cape of Good Hope.

TABLE XXV.

Class 2 B.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ and Ammonia.	SnCl ₂ + HCl.	Deal Shaving and HCl.	N ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.
English Oak (<i>Quercus Ilex</i>).	Blue-black (green with excess).	Pp.	Reacts somewhat.	Slight pp. Dark brown pp.	No reaction.	Faint reaction.	Reddens.	Crimson, dilutes pink.	Reddish-brown pp.
Jaft or Delift. ¹ Sapped oak product.	Blue-black pp.	Pp.	Reacts red-blue.	Brown pp. Dark brown pp.	No reaction. Dark brown pp.	Do.	Some darkening.	Do.	Do.

¹ A Persian product, dark smokes very rich in tannin (about 40 per cent.). Strong infusions dry whitish and iridescent.

TABLE XXVI.

Class 8 a.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SuO ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.
Alpen galls (of <i>Quercus myfectoria</i>).	Blue-black pp.	No pp., slight scum.	Reacts red to blue.	Dark pp., insoluble.	Light yellow pp.	No reaction.	No reaction.	Greenish to dirty yellow.	Pale pp., turning bluish green.
Sumach (leaf of <i>Rhus coriaria</i>).	Do.	No pp.	Reacts feebly.	Dark-brown in-soluble pp.	No reaction.	Do.	Do.	Yellow.	Yellow pp., turning bright green.
Myrobalans (<i>Ternstroemia chelonoides</i>).	Do.	Do.	Reacts red to blue.	Dark in-soluble pp.	Do.	Do.	Yellow.	Do.	Yellow pp., turning greenish.
Pomegranate rind (<i>Punica granatum</i>).	Do.	Do.	Do.	Dark-brown in-soluble pp.	Do.	Do.	No reaction.	Orange-brown.	Bright yellow pp., turning red with excess.
Algarobilla (pod of <i>Cassipouia brevifolia</i>).	Do.	Do.	Do.	Dense dark pp.	Do.	Do.	Deep yellow.	Deep yellow-brown.	Bright yellow pp., darkens somewhat.
Divi - Divi (pod of <i>Cassalpinia coriaria</i>).	Do.	Do.	Do.	Do.	Do.	Do.	No reaction.	Crimson.	Yellow pp., turning red-purple.
Algaroba (probably pod of <i>Prosopis juliflora</i>).	Do.	Do.	Reacts red to olive.	Do.	Do.	Do.	Yellow.	Yellow to olive.	Yellow pp., turning black.
Valonia (cup of <i>Quercus agrifolia</i>).	Do.	Do.	Reacts red to blue.	Dark reddish pp.	Do.	Do.	Purplish pink.	Deep yellow.	Yellow pp., turning red-purple.
“Oakwood” extract (oak or chestnut wood)	Do.	Do.	Do.	Purple-brown pp.	Do.	Do.	Reddens.	Yellow-brown.	Do.

¹ Dyes yellow on Si mordants.

² Moderately strong potassium nitrate solution precipitates divi, but not *divi* oakwood solutions; pp. soluble in hot, or much cold water.

³ Crude chestnut wood extract may be discoloured, from oakwood by its violet reaction with ammonium sulphide (see *Gerber*, No. 260, p. 155).

TABLE XXVII.

Class 3 β.	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ and Ammonia.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.
Pure galloic acid.	Blue-black pp.	No pp.	No reaction.	Dark pp.	No reaction.	No reaction.	No reaction.	Yellow.	Pale pp., turning blue. Pink colour, no pp.
Bahoi Jods (<i>Acanthia arabica</i>).	Blue-black.	Do.	No reaction, darkens.	Dark green colour.	Do.	Faint violet.	Do.	Reddish-violet.	

TABLE XXVIII.

	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ and Ammonia.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.
Catechol.	Dark green coloration.	No pp.	Turns yellow.	Green colour.	No reaction.	No reaction.	No reaction.	Green coloration.	No pp.
Protocatechuic acid.	Do.	Do.	Turns brown.	No pp.	Do.	Do.	Do.	No reaction.	Do.
Phloroglucol.	No reaction	Bulky white pp.	Turns olive-green.	Do.	Do.	Red-violet coloration.	Do.	Slight yellow.	Do.
Pyrogallol.	Blue-black, turning green and brown.	No pp.	Turns yellow.	Brown colour.	Do.	No reaction.	Do.	Brown coloration.	Violet coloration, rapidly turning brown.
Gallic acid.	Blue-black coloration.	Do.	Turns brown.	Do.	Do.	Do.	Do.	No reaction.	White pp., rapidly turning blue.

TABLE XXIX.—REACTIONS OF PROFESSOR TRIMBLE'S PURIFIED OAK BARK TANNINS.
(A Monograph of the Tannins, vol. ii, p. 86.)

	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ and Ammonia.	SuCl ₂ + HCl.	Dead Shavings and HCl.	Na ₂ SO ₃ .	Lime Water.
Black oak (<i>Q. tinctoria</i>) or Quercitron.	Green colour and pp.	Yellow pp.	Brownish yellow pp. Pinkish colour, changing to brown pp.	Green colour.	Yellow with some pink. Pink colour.	Violet colour.	Yellow colour.	Pp. turning pink, then red. Do.
Pin oak (<i>Q. palustris</i>).	Do.	Do.	Brown pp.	Brownish-green colour.	Pinkish colour.	Do.	Pink colour.	Do.
Scarlet oak (<i>Q. coccinea</i>).	Bluish-green colour.	Do.	Brown pp.	Green colour.	Pinkish yellow colour.	Do.	Pinkish-yellow colour.	Pp. turning reddish.
Spanish oak (<i>Q. falcata</i>).	Green pp. and pp.	Do.	Do.	Red-brown pp.	Yellow colour, some pink.	Do.	Yellow with pink streaks.	Do.
White oak (<i>Q. alba</i>).	Do.	Do.	Do.	Brown-green colour.	Pinkish colour.	Do.	Pinkish colour.	Pp. turning pink.
Willow oak (<i>Q. phellos</i>).	Do.	Do.	Do.	pp.	Very yellow colour.	Do.	Yellow with pink streaks.	Pp. turning green, liquid reddish.
Chestnut oak (<i>Q. prinus</i>).	Do.	Do.	Do.	Red-brown pp.	Do.	Do.	Do.	Pp. turning pink.
Swamp white oak (<i>Q. bicolor</i>).	Do.	Do.	Do.	No pp. Greenish-brown colour.	Do.	Do.	Do.	Do.
English oak (<i>Q. robur</i>).	Bluish-green colour.	Do.	Pink colour, changing to brown pp.	pp.	Decided pink colour.	Do.	Pink colour.	Do.
Indian oak (<i>Q. semicarpifolia</i>).	Green pp. and pp.	Do.	Brownish-yellow pp.	Red-brown pp.	Pink colour.	Do.	Yellow colour.	Do.

TABLE

The following table is given by Andreaesch¹ for alcoholic solutions,* and the reagents were always added in excess, and the mixture allowed no visible change takes place.

Reagent.	Spruce Bark.	Oak bark.	Willow bark.	Mimosa Bark.	Hemlock Bark.	Oakwood.
Water, . . .	Orange turbidity.	Yellow white pp., partly soluble.	Greenish turbidity.	Yellow-white pp., brown solution.	Dark red-brown pp.	Light yellow turbidity.
Hydrogen peroxide.	As above.	Yellow-white pp., partly soluble.	Apple-green pp.	As above.	Light brown pp. and soln.	Yellowish-white flocculent pp.
Hydrochloric acid.	Red-brown solution.	Yellow-brown pp., brown solution.	Yellow white pp., rose-red zone.	As above.	Dark brown pp. and solution.	Pale buff flocculent pp.
Sulphuric acid.	Rust-brown pp. and solution.	Yellow-white pp., brown solution.	Yellow brown pp., cherry-red zone.	Slight rust-brown pp., dark solution.	Dark rust-brown solution.	Brown pp. and solution.
Nitric acid, . . .	Yellow brown pp., dark brown solution.	As above.	Yellow pp. and solution.	As above.	Red-brown pp. and solution.	Yellow flocculent pp.
Acetic acid, . . .	Yellowish-white pp.
Ammonia, . . .	Brown pp., partly soluble in excess.	Dark yellow pp., soluble in excess.	Turbidity.	Violet-red pp., soluble in excess.	Dark brown pp., insoluble in excess.	Pp. soluble to red solution in excess.
Chloroform, . . .	Yellow-red flocculent pp., brown solution.	Yellow-white pp., yellowish solution.	Whitish turbidity.	Dark brown deposit.
Ethyl-ether, . . .	Light brown pp.	Light yellow pp.	...	Grey-violet pp.	Brown pp.	Slight yellowish-white pp.
Acetic ether, . . .	Turbidity.
Benzol, . . .	Reddish-brown sediment.	Brown flocculent pp.	...	Reddish-black layer below.	Brown layer below.	Slight red-brown pp.
Petroleum ether.	Ether not coloured.	Ether pale-yellow.	Ether faint red.	...
Carbon disulphide.	CS ₂ yellow.	CS ₂ yellow.	CS ₂ green.	CS ₂ pale yellow.
Naphthol, . . .	Brown pp. and solution.	Brown pp. and solution.	Yellow-brown pp., dark red-brown solution.	Brown pp. and solution.	...	Yellow-brown pp., dark solution.
Glycerin, . . .	Yellow flocculent pp.	...	Greenish-white flocculent pp.	...	Red flocculent pp.	Slight turbidity.
Tartaric acid, . . .	Whitish-yellow turbidity.	Slight whitish-yellow pp.	Yellow-green flocks.	Yellow-brown pp.	Red-brown pp.	Whitish-yellow flocculent pp.
Citric acid, . . .	As above.	As above.	As above.	As above.	As above.	As above.
Oxalic acid, . . .	As above.	As above.	As above.	As above.	Voluminous red-brown pp.	As above.
Trinitrophenol.	Yellow pp. and solution.	Yellow-brown pp.	...

¹ Gerber, 1894, p. 195, and Procter (*loc. cit.*).

XXX.

may* be used for the examination of alcoholic extracts of leathers. to stand over night. Where spaces are left blank it is understood that

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach.	Knopporn.	Birch Bark.
Turbidity.	Dirty yellow turbid over dark zone.	Dirty yellow turbidity.	Marked yellow-brown turbidity.	Dirty green pp.	Yellow-white pp.	Yellow-brown turbidity.
Brown-yellow flocculent pp.	As above.	Yellowish pp.	Yellowish pp.	Green pp.	As above.	Rusty brown pp.
As above.	Light brown turbidity.	Light brown turbidity.	Whitish-yellow pp.	Dark green pp.	As above.	Yellow-brown pp.
Dark red solution.	Slight yellow pp., pale solution.	Slight yellow-brown turbidity.	Dirty reddish pp.	Light green pp., green solution.	Yellow-grey pp.	Dense red-brown pp., dark solution.
Slight pp., red-brown solution.	Slight pale pp., dark solution.	Dull red coloration.	Dirty brown turbidity.	Dark green pp.	Dark yellow pp.	Red-brown pp. and solution.
...	Yellowish turbidity.	Dark yellow turbidity.	Light brown turbidity.	Dull dark green pp.	Yellow-brown pp.	...
Dark red-brown pp.	Yellowish pp., partly soluble, reddens.	Yellowish pp., turns brown, sol. in excess.	Pale yellow pp., partially soluble, in excess, turns brown.	Pale green pp., darkens.	Dense greyish-white pp., reddening.	Dark flesh-red pp., soluble in excess.
Solution pale yellow, above red-brown.	Yellow-grey flocks.	Yellow flocks.	Yellow-brown flocks.	Slight green deposit.	Dense yellow-white pp.	Slight brown pp.
...	Grey-brown pp.	Trace flesh-coloured pp.
...
...	Dirty white pp., turning dark brown.	Pale yellow flocks.	Rust-brown pp.	Slight yellow pp. on long standing.	Reddish-yellow flocks.	...
...	Ether yellow-green.	...
...	Dense yellow flocks at zone.	CS ₂ scarcely coloured, yellow flocks at zone.	CS ₂ scarcely coloured, yellow flocks at zone.	CS ₂ coloured green.	CS ₂ coloured yellow-green.	...
Yellow-brown pp., dark solution.	Slight yellow-brown pp.	Slight yellow-brown pp.	Slight yellow-brown pp.	Green-brown pp.	Slight greyish pp. on long standing.	Yellow-brown pp., dark red solution.
...	Long standing yellowish pp.	Long standing yellow flocks.	Long standing slight turbidity.	Long standing dark green pp.	Slight turbidity.	Turbidity.
Yellow-brown flocculent pp., dark red solu.	Yellow-grey pp.	Yellowish pp.	Yellowish pp.	Greenish pp.	Yellow-green pp.	Light rust-brown pp.
As above.	As above.	As above.	As above.	As above.	As above.	As above.
As above.	Sulphur yellow pp.	As above.	Yellow-brown pp.	As above.	As above.	As above.
...	Brown-yellow pp., turns lemon.	Yellow-brown pp., turns yellow.	Turbidity first reddish, then yellow.	Apple-green pp.

TABLE FOR ALCOHOLIC

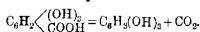
Reagent.	Spruce Bark.	Oak bark.	Willow Bark.	Mimosa Bark.	Hemlock Bark.	Oakwood.
Salicylic acid,	Light brown pp.	Yellow-white flocculent pp.	Greenish-yellow pp.	Slight brown pp.	Bulky red-brown pp.	Yellow-white pp.
Tartar emetic,	Fawn-coloured pp.	Greyish-yellow pp.	Greenish-white pp., deep green layer above.	Violet-red pp.	Dirty brown pp.	As above.
Potassium ferro-cyanide.	Yellow-white pp.	Yellow-white pp.	Green-white pp.	Flesh-red pp.	Red-brown pp.	Slight white pp.
Potassium sulpho-cyanide.	Yellow-brown flocculent pp., sol. on heating.	Yellow-brown flocculent pp.	Leaf-green pp.	Chocolate pp.	Red-brown pp., sol. on heating.	Yellow-white pp., pale yellow solution.
Potassium cyanide.	Pale-brown turbidity.	Pale-brown turbidity.	Leaf-green pp., yellowish sol.	...	As above.	Pp. brown below, yellow-white above.
Lime, . . .	Yellow-brown pp., glittering on surface.	Pp. yellow-brown below, chocolate above, yellow solution.	Dirty sulphur-yellow pp.	Violet-blue pp., brown above.	Violet-brown pp., dull brown and glittering above.	Pp. white below, above blue, later brown.
Baryta, . .	Dirty yellow pp., yellow-white solution.	As above.	As above.	Blue-green pp., brown above.	As above.	Blue pp. turning brown glittering red-brown above.
Strontia, . .	As above.	As above.	As above.	Dirty blue pp.	As above.	Pp. white below blue above, turning brown.
Magnesia, .	Light-brown pp.	Dirty white pp.	Violet-red pp., green solution.	Grey pp.	Red pp.	Yellow-white pp.
Potassium chromate.	Dull brown pp.	Yellow-brown pp.	Bright yellow pp.	Brown pp.	Brown pp.	Green-brown pp., turning brown.
Mercuric chloride.	Light red brown pp.	Yellow-white turbidity.	White pp.	Light-reddish blue pp.	Blood-red pp.	Yellow-white flocculent pp.
Mercurous nitrate.	Dirty grey-brown pp.	Pp. reddish-yellow turning brown.	Dirty yellow pp. on long standing.	Dirty brown pp.	Red-brown pp., turning dull brown.	Brick-red pp., turning brown-red or yellow-grey.

SOLUTIONS—*continued.*

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach.	Knooppenn.	Birch Bark.
Brownish-yellow pp., dark red-brown liquid.	Greyish-yellow pp.	Yellowish pp.	Yellow-brown pp.	Green pp.	Greyish-yellow pp.	Pale rust-brown pp.
Fawn-coloured pp.	Pale grey-yellow pp.	Cream-coloured pp.	Ochre-yellow curdy pp.	Yellow-green curdy pp.	Dirty white curdy pp.	Bulky pale rusty pp.
Pale red-brown pp.	Pale yellow pp.	Cream-yellow pp.	Orange pp.	Pale green pp.	Yellow-green pp.	Bulky pale rusty pp.
...	Yellow-grey pp.	Yellow pp.	Dark yellow pp.	Green pp.	Orange-yellow pp.	Turbidity.
Slight pp. amaranth-red solution.	As above.	As above.	As above.	As above.	Curdy reddish-white pp., darkens on standing.	Yellow-white pp., dull brown and glittering above.
Violet-brown p., dark brown above.	Pale chocolate pp.	Bright yellow pp., colourless solution.	Cream-coloured pp., which darkens.	Green pp., turning yellow.	Olive brown pp.	Flesh-red or scarlet pp.
Grey-white pp., glittering, chocolate-brown above.	As above.	As above.	As above.	Green pp., turning sulphur-yellow.	Green pp., turning grey-brown over night.	Grey-white pp., brown above.
As above.	Chocolate pp., turning black.	Dirty green pp., turning brown.	Pale red pp., dirty grey above.	As above.	As above.	Greyish-white pp., vermillion above.
Violet pp., dark solution.	Yellowish pp.	Yellowish pp.	Grey-brown pp.	Dirty green mass.	Yellow-white pp.	Pale flesh col. pp.
Dark, dull brown pp.	Yellow-brown pp.	Dirty brown pp.	Dark brown pp.	Dirty brown pp.	Dark red-violet pp., turning chocolate.	Chestnut-brown pp.
Dark turbidity.	Dirty yellow pp., partly soluble.	Yellow-brown pp., solution in excess.	Brown pp., mostly sol. in excess.	Dirty green pp., part soluble in excess, turns yellow.	Yellow-green pp.	Reddish-yellow pp.
Chocolate pp. on long standing.	Orange-yellow pp., turning dirty grey.	Orange-yellow pp., turning dirty yellow.	Orange-yellow pp., turning dirty yellow.	Grass-green pp.	Orange pp., turning grey.	Grey pp.

Catechin is a crystalline substance which is frequently deposited from catechol tan liquors, and separates very readily from solutions of gambier. It may be purified by recrystallisation from hot water. Its melting point is from 204°–205°. It is oxidised by potassium permanganate, and may be estimated by titration of the filtrate after removal of the tannin with gelatine, as in the Löwenthal method. It is also absorbed to a certain extent by hide powder. Fused with caustic alkali, it first gives proto-catechuic acid and phloroglucol, but with further heating, catechol.

Pyrogallol, $C_6H_3(OH)_3$, is made by heating gallic acid alone, or with water, in a sealed tube to a temperature of 210° C.



It is a white crystalline substance melting at 115° C. and subliming when carefully heated. It is readily soluble in water and with difficulty in alcohol and ether. In alkaline solution it rapidly absorbs oxygen from the air with the production of a deep brown coloration. It reduces salts of mercury, silver, and gold, being itself oxidised to acetic and oxalic acid. With lead acetate it gives a white precipitate, having the composition $C_6H_6O_3PbO$.

Phloroglucin, an isomer of pyrogallol, is prepared by fusing resorcinol $C_6H_4(OH)_2$ with caustic soda. It crystallises in prisms containing two molecules of water, and is readily soluble in water, alcohol, and ether. It is not precipitated by lead acetate, and with iron salts it gives a violet coloration.

Catechol, $C_6H_4(OH)_2$, is produced by the dry distillation of certain tannins, or by fusing catechin with sodium hydrate. It is a crystalline compound melting at 111° C., and readily soluble in water, alcohol, and ether. Its aqueous solution gives a precipitate with lead acetate. It gives a dark green coloration and ultimately a black precipitate with ferric salts, such as iron alum.

Gallic Acid, $C_6H_2(OH)_3COOH$, is produced by the hydrolysis of digallic or gallotannic acid when acted upon either by dilute acids or alkalis or ferments. It is therefore frequently found in natural tannins containing gallotannic acid. It is absorbed by hide powder in the bell filter, but is not precipitated by collin. It is readily soluble in ether, and is oxidised by permanganate of potash. It may be separated from tannic acid by means of collin or by treating a mixture of the two with lead acetate and acetic acid, when the lead gallate dissolves, leaving insoluble lead tannate. Its chief reactions are—

Bluish-black coloration with ferric chloride.

Precipitation of silver, gold, and platinum from solutions of their salts. Heated at 140° C., with four parts of strong sulphuric acid, rufigallic acid, a dark red substance, is formed, and precipitated on dilution with water. Mild oxidising agents—silver hydroxide, arsenic oxide, iodine, and water—convert gallic into ellagic acid. With acetyl chloride it forms a triacetate

which crystallises from alcohol in needles. Aqueous solutions of picric acid containing excess of ammonia turn red, changing to green on the addition of gallic acid.

Tannic or Digallic Acid, $C_{14}H_{10}O_9 + 2H_2O$, is very widely distributed in nature. It may be prepared artificially by oxidising gallic acid with silver nitrate, or by heating it with phosphorus oxychloride to $130^\circ C$. or by boiling with dilute arsenic acid. When boiled with dilute acids or alkalis the reverse action takes place, gallic acid being reproduced,



It may be prepared from gall nuts by extracting with ether and alcohol. The lower layer is extracted with ether to remove gallic acid, after which the tannic acid is salted out and made into the lead salt, this being decomposed by sulphuretted hydrogen.

Pure tannic acid is a colourless amorphous powder, readily soluble in water and alcohol, but only very slightly in ether. It forms insoluble tannates with many metals, such as lead, copper, and calcium, and also with organic bases, such as the alkaloids. Commercial tannic acid may be valuated by the processes described in Chapter IX. Its chief impurity is gallic acid, from which it can be freed by repeated extraction with ether.

Ellagic Acid ($C_{14}H_8O_6$).—Many tannins, such as valonia, etc., when allowed to stand give an insoluble precipitate known as bloom or ellagic acid. This acid may be prepared by extracting such tannins as *divi divi* with alcohol and precipitating by pouring the extract into water. The precipitate is then collected and recrystallised from alcohol. It may be estimated in tanning materials by the process given for valonia.

Ellagic acid probably exists in tannin materials as ellagitannic acid which is readily hydrolysed into insoluble ellagic acid.

Properties.—Yellowish powder containing one molecule of water of crystallisation. Insoluble in water. Soluble in hot alcohol to a yellow solution. The powdered substance gives with ferric chloride a green coloration changing to black. Treated with nitric acid containing nitrous acid it gives a blood-red coloration, a property also possessed by flavo-ellagic acid, another oxidation product of gallic acid, which A. G. Perkin has obtained by treating it with potassium persulphate and dilute sulphuric acid.

Phlobaphenes, or insoluble reds.—These bodies are anhydrides of tannic acids and are often found in extracts of tanning materials. Thus most catechol tannin solutions when allowed to stand or boiled give rise to these bodies. They are only slightly soluble in water, but combine with skin substances and produce colour in the leather.

Protocatechuic Acid, $C_6H_5(OH)_2COOH$, is a further decomposition product of the catechol tannins. When the phlobaphenes or red anhydride bodies obtained from these tannins by fermentation or boiling with acid are

fused or even boiled with potash, protocatechuic acid is generally found in the resulting mixture. It is a di-hydroxybenzoic acid and bears the same relation to catechol that gallic acid does to pyrogallol.

Properties.—Colourless plates or needles containing one molecule of water. Easily soluble in hot water, alcohol and ether; melts at 109° C., but loses its water of crystallisation at 100° C. With ferric chloride it gives a green coloration, changing to blue with very dilute soda, and finally to red. Ferrous salts colour its solution violet. It reduces ammoniacal solutions of silver salts, but has no action on Fehling's solution.

Preparation of Tannins.—Tannic acids may be extracted from natural tannins by treatment with a suitable solvent, such as acetone.

Trimble recommends the following method:—The material is extracted with acetone, which is evaporated off, the residue is dissolved in water to precipitate anhydrides and colouring matters. The solution is again filtered and shaken out with acetic ether, the solvent being evaporated under reduced pressure. Procter (*L.I.L.B.*, p. 43) gives the following method.

The material is extracted with ether containing some water and alcohol. The liquid separates into two layers, the lower containing fairly pure tannin dissolved in water and alcohol, the upper containing gallic acid. The lower layer is removed by a separating funnel and extracted with ether to remove all traces of gallic acid, after which the tannic acid may be rendered insoluble by saturating with common salt. Or the tannic acid solution may be treated with lead acetate in successive small quantities. The first and last portions of the precipitate are rejected. The acids are collected, suspended in water and decomposed with sulphuretted hydrogen. The hot sulphide is filtered off and the excess of sulphuretted hydrogen boiled off, after which the liquid is again extracted with ether and the tannic acid afterwards shaken out with acetic ether and evaporated. Having obtained the tannins in a moderately pure condition they are then examined by boiling with acids, fusion with alkali, and dry distillation.

(1) *Action of Acids.*—Many natural tannins are glucosides, and these, when boiled with dilute acid, still yield glucose as one product. Others yield insoluble reds, gallic or ellagic acids.

(2) *Fusion with Alkali.*—The tannin is carefully fused with alkali, after which the latter is dissolved out with sulphuric acid, the excess of sulphuric acid neutralised and the products of fusion extracted with ether. Phloroglucol may always be recognised by its reaction with deal shavings; the latter treated with a solution containing phloroglucol and afterwards with strong hydrochloric acid on warming become deep violet in colour.

Protocatechuic acid is recognised by its colour reactions.

Decomposition by Heat.—The tannin is carefully heated in a small

retort and the products of distillation examined primarily for catechol and pyrogallol.

Thorpe (*L.I.L.B.*, p. 50) recommends the following process :—“ 1 gm. of the substance is heated with 5 c.c. of pure glycerine to 160° C., the temperature slowly raised to 200°–210° and maintained at this temperature for 30 minutes. After cooling, about 20 c.c. of water is added and the liquid shaken with a volume of ether without filtration. The ethereal layer, which may contain pyrogallol, phloroglucol, and catechol, is separated from the aqueous layer, evaporated to dryness, and dissolved in 50 c.c. of water.” The solution is then tested by colour reactions.

An unknown tannin may also advantageously be tested for its weight-giving and colour-producing properties by Parker's method, as described in Chapter IX.

CHAPTER IX.

THE ANALYSIS OF TANNING MATERIALS.

It is unfortunately impossible to take a tanning material and separate and estimate the tannins it contains with absolute accuracy, chiefly on account of the fact that, on the one hand, tannins are usually of mixed origin, and, on the other, no body is known which will quantitatively precipitate them, to the exclusion of all other bodies. Even if the latter were possible it is doubtful if the result obtained would be of very much use to the tanner, since other points, such as weight-giving properties and colour, have also to be taken into consideration.

Although the exact analysis of tanning materials presents so many difficulties, yet an immense amount of work has been devoted to the subject, and methods of analysis have been worked out which, in competent hands, are capable of giving consistent and reliable results, and which are, in fact, in their way, models of empirical accuracy. It is, however, necessary to emphasise the fact that they are entirely empirical, and that in consequence success in carrying them out depends upon the correct observance of the conditions of experiment prescribed. Although standardisation of method is not in all cases to be desired owing to the limitations which it puts upon individuality, yet in this instance it has been attended with much success, and the example of the I.A.L.T.C. might advantageously be followed in other directions. The chief objection which can be urged against the methods adopted for the analysis of tanning materials is that they are indirect and that the percentage of tannins present is estimated by difference. A method to be scientific must depend upon the precipitation of a known compound of tannic acid by means of a constant and well-defined precipitant, and the precipitate produced must be capable of being directly weighed or titrated and its exact composition also determined. Such a method is rendered extremely difficult to find by the fact that in no known tanning material is the active substance a single acid. In nearly all cases they contain two or more of the known forms of tannic acids. In the standard method of analysis most of these acids are co-estimated with tannic acid, it being assumed that they form leather. This assumption is, however, not quite warranted, and much remains to be done in the elucidation

tion of this point. When it is accurately known which particular tannic acid the tanner requires, the problem will be much simplified, and a method will doubtless be found to replace the present official hide-powder process. A step in the direct method of analysis has been made by Messrs Parker and Payne in their Collin process, and by Crouzel, Trotman and Hackford, who used antipyrin and strychnine respectively. Before describing the methods employed by the Association, a short *résumé* will be given of some of the other methods which have been proposed, many of which are of considerable importance, the more important ones being subsequently described in greater detail.

(1) **Precipitation with Gelatine**—and weighing the precipitated leather or determining the percentage of nitrogen it contains by Kjeldahl's process.

Although gelatine is of much use in removing tannic acid from solutions, yet the precipitate is of too uncertain a composition for reliable results to be obtained from its estimation. The process, however, may be somewhat improved by using a standard gelatine solution and making it volumetric by filtering a small quantity of the liquid and observing whether the further addition of gelatine solution causes a precipitate.

(2) **Precipitation of Tannins by Metallic Salts**.—Ferric, zinc, antimony and copper salts have all been employed with varying success. Ammonia and copper sulphate solution have been used, but it is quite evident that they are capable of only a very limited application, since many tannates are readily soluble in excess of ammonia and all in the liberated acid. This method may, however, be used for the separation of different tannins in some cases. Thus all those tannins whose copper salts are insoluble in ammonia may be separated from the large class whose tannates are soluble.

In the process of Richards and Palmer a standard solution of tartar emetic is prepared containing 6.73 grms. per litre (1 c.c. = .01 gm. digallic acid). The solution is run into the tannin solution, to which ammonium acetate is added, to assist the settling of the precipitate, till the tannin is all thrown down, the end point being found by placing a drop of the supernatant liquid on a tile with a drop of sodium sulphide solution. The presence of antimony in the liquid is indicated by a red coloration due to the formation of antimony sulphide.

(3) **Precipitation by means of Iron** (*Zeit. anal. Chem.*, 1902, xli., 717-734, and *Analyst*, 1903, p. 117). The following solutions are required:—Seminormal carbonate of soda and ferric sulphate, and a solution of 5 grms. of sodium tartrate in a litre of 6 per cent. acetic acid. When 10 c.c. of the first two solutions are boiled together and filtered the filtrate must not give an alkaline reaction with methyl orange, and when 10 c.c. of each solution are diluted with 50 c.c. of water and 25 c.c. of the tartrate solution are added and the whole boiled for 5 minutes, it must remain perfectly clear. The strength of the tannin solutions

should not be more than 0.4 per cent. For a tannin determination, 50 c.c. of the tannin solution are shaken with 10 c.c. of the sodium carbonate and iron solutions, and then immediately mixed with 25 c.c. of the tartrate solution and shaken. It is then boiled for a minute and filtered, and the filter washed with hot water, dried, ignited, and weighed. The weight of the precipitate multiplied by 4.024 gives the amount of the tannin in the 50 c.c. taken. Gallic acid gives no precipitate when treated in this way.

(4) Since tannins are usually destroyed by oxidising agents, many methods for their estimation founded on this fact have been suggested, one of which (Löwenthal's method) is of considerable importance.

(5) **Measurement by Means of direct Oxygen Absorption.**—Thompson (*Analyst*, 1903, p. 43) proposed to treat the tannin with a measured quantity of hydrogen peroxide solution in the presence of sodium hydroxide. After absorption was complete the excess of peroxide is decomposed by means of lead peroxide and the liberated oxygen measured. One gram. of tannin absorbs 20 c.c. of oxygen at 0° C. and 760 mm. pressure.

(6) **Iodometric Method of determining Tannic and Gallic Acid** (Jean, *Analyst*, 1900, p. 127).—This is based on the fact that iodine combines with tannic or gallic acid to form compounds which do not give a blue coloration with starch. A solution of iodine in potassium iodide is prepared and standardised separately with 0.1 per cent. solution of tannic and gallic acid dried at 100° C. For this purpose 20 c.c. of the 0.1 per cent. solution are mixed with 5 c.c. of concentrated sodium bicarbonate solution and the iodine run in drop by drop with stirring till the liquor gives a blue coloration when applied to starch paper. The iodine solution is then adjusted in strength so that 10 to 10.5 c.c. are equivalent to 10 c.c. of the tannin solution. Gallic acid requires about 3 c.c. more of the iodine solution than tannic acid. A correction must be made for the sodium bicarbonate (generally about 0.4 per cent. and is determined by experiment). Jean extracts tannin substances by heating about 1 gram. of the powdered sample for half an hour with 15 c.c. of water at 50° C. The extract is then decanted and the residue boiled with a little more water and again decanted, the process being continued till the material is completely exhausted, when the solution is cooled and made up to a definite volume.

Ten c.c. of the solution are then titrated with the iodine as described above, the dilution being repeated till the amount corresponding to 10 c.c. of the iodine solution is ascertained, when the total amount of astringent matter is calculated. For the separation of the tannin a solution of albumen is prepared by making 2 grms. of dried egg-albumen into a paste with glycerine, and after standing for 30 minutes making up to 1000 c.c. with warm water. The solution may be preserved by means of a little camphor.

Fifty c.c. of the tannin extract are mixed with 15 c.c. of albumen and

20 grms. sodium chloride, the mixture made up to 100 c.c., mixed and filtered, the first portions of the filtrate being rejected. A volume of the filtrate equal to double that required in the first titration is acidified with a drop of acetic acid and boiled to coagulate excess of albumen. The filtrate and washings from this precipitate are cooled and mixed with 9 c.c. of the sodium carbonate solution and titrated with the standard iodine solution. The albumen must be titrated alone in a blank experiment and the correction found (generally 0.7 c.c.) applied. The gallic acid is calculated from the difference in the two titrations.

The method is capable of only limited application and has not given reliable results in the author's laboratory. It is evident that it is inapplicable in the case of sulphited preparations. When amylaceous substances are present, Jean states that the extraction may be made with alcohol instead of water.

Boudet (*Bull. Soc. Chim.*, 1906, xxxv., 760-762, and *Analyst*, 1906, 370) gives the following improved method. He treats the tannic acid solution with excess of iodine and titrates back the excess, 1 gm. of iodine combining with 1.137 grms. of pure tannic acid. The reagent is prepared by dissolving 4 grms. of iodine and 8 grms. of potassium iodide in a litre of distilled water; a thiosulphate solution containing 7.81 grms. per litre is also prepared. A quantity of the solution containing about 5 grms. of tannic acid is allowed to stand with 10 c.c. of the iodine solution for two hours, after which the excess is titrated back with the thiosulphate solution.

(7) **Precipitation by means of Organic Bases.**—The following are among those employed with more or less success:—

(a) *Precipitation by means of Antipyrin* (E. Crouzel, *Ann. Chim. anal. Appl.*, vii. 373-374).—E. Crouzel found that tannic acid in solution gives a precipitate with antipyrin, while gallic and other vegetable acids do not. The tannic acid is precipitated with excess of the reagent, sodium bicarbonate added, the precipitate collected on a filter, washed, dried at 100° C. and weighed. It contains 50 per cent. of tannin.

(b) *Precipitation by Analgesin* (Crouzel, *J.S.C.I.*, 1902, p. 992).—The tannin under examination is dissolved in water and analgesin added until no further precipitate is produced, and the amount of tannic acid estimated from the weight of the precipitant employed, or the precipitate is filtered on to a tared filter, washed, dried at 100° C., and weighed. When it is difficult to determine the end of the reaction an excess of the reagent is added and some sodium bicarbonate, which causes the precipitate to settle sharply. This process is interesting as an attempt to separate the tannate compound of tannic acid, but experiments made in the author's laboratory prove that the insolubility of the precipitate is not sufficient to render the process of much practical use.

(c) *Precipitation by means of Alkaloids.*—Parker and Payne have made experiments in this direction with quinine acetate, and have given a

preliminary note stating that a method of titration has been worked out, their object being to confirm results obtained by their Collin process. The reaction between alkaloids and tannic acid has also been investigated by Trotman and Hackford (*J.S.C.I.*, 1905, 1097), who find that strychnine tannate is highly insoluble and may be successfully used in the estimation of tannic acid, or tannic acid in tanning materials. The precipitated compound has the formula $C_{21}H_{22}N_2O_2C_{14}H_{10}O_9$. They further found that gallic acid is not precipitated with the tannic acid. Excess of a dilute alcoholic solution of the alkaloid is added to the tannic acid solution, and the precipitated tannate filtered and weighed in a Goch crucible.

(8) **Volumetric Process by means of Saffranine** (Specht and Lorenz, *Analyst*, 1900, p. 163).—This process depends upon the precipitation of saffranine as a tannin antimony lake, using an excess of the dye and determining that excess by titration with standardised hydrosulphite.

(9) **Absorption of Tanning by means of Silk** (Vignon, *Analyst*, 1899, p. 137).—Ungummed silk in the proportion of 5 grms. to 0.1 gm. of tannin is immersed in a solution of tannin for 5 hours at 50° C., at the end of which time the whole of the tannin is absorbed and may be subsequently estimated by titration with permanganate. According to the author the absorption is more rapid than with hide powder, and no soluble organic matter goes into the solution. The colour of the silk at the end of the absorption gives a useful indication of the colour value of the tanning material.

(10) Several processes have been proposed depending on the power which tannic acid possesses of precipitating basic colouring matters, but none have survived criticism. Many of the above methods give good results when applied to solutions of pure tannic acid, but break down when applied to tannic materials. The following processes have all been applied more or less successfully to the analysis of mixed tannins.

(11) **Löwenthal Method**.—This method, depending on the oxidation of tannin by potassium permanganate, gives excellent results with solutions of pure tannic acid and accurate comparative results with extracts of tannin materials.

The following solutions are required:—

- (1) Standard potassium permanganate solution.
- (2) Indigo carmine solution.
- (3) Saturated solution of sodium chloride and sulphuric acid.
- (4) 3 per cent. solution of gelatine.

These solutions are prepared as follows:—

Permanganate Solution.—Five grms. of finely-powdered permanganate are dissolved in a litre of water, the resulting solution being retained as a stock solution. For use it is diluted to one-fifth of its strength. In order to standardise it, take 50 c.c. and dilute to 250 c.c. with distilled water, and titrate with a standard solution of tannin and indigo carmine. The

tannic acid solution must be freshly prepared and the water simultaneously estimated in a portion of the sample and due allowance be made.

About 3 grms. of tannin dissolved in a litre of distilled water gives approximately the most suitable strength solution.

Ten cubic centimetres of this solution are placed in a large porcelain dish of about a litre capacity, and 20 c.c. of indigo carmine solution added and 750 c.c. of water; the diluted permanganate is then run in from a burette with constant stirring till the faintest indication of pink is observed at the edge of the liquid against the sides of the dish. It is most important that the permanganate towards the end of the reaction be only added in small quantities and that sufficient interval be allowed between each addition for complete oxidation, otherwise the end point is easily over-reached. The volume of permanganate necessary to decolorise the tannin and indigo carmine having been found, a blank experiment is performed in exactly the same way with the indigo carmine alone, the difference between the two readings being the volume of permanganate required by the tannin, from which the exact equivalent of the solution can be calculated. The following example will show the method of calculation:—

Tannic acid solution 0.5 grms. in 100 c.c. distilled water.			
On titration with diluted permanganate (1 in 5)			
5 c.c. tannic solution + 20 c.c. indigo carmine	=	19.8	c.c. dilute permanganate.
20 c.c. indigo carmine	=	9.8	„ „ „
∴ 5 c.c. tannic acid solution	=	10.0	„ „ „
∴ 1 c.c. permanganate	=	0.0025	gm. tannic acid.

Indigo Carmine Solution.—Five grms. of indigo carmine are made into a paste in a mortar with a little water and made up to a litre with dilute sulphuric acid, after which the solution is filtered. Its strength should be such that 20 c.c. are decolorised by about 25 to 30 c.c. of permanganate solution, and if necessary its strength must be adjusted to this point.

Earp (Collegium, 1906, p. 92) recommends synthetic soluble indigotin manufactured by the Badische Anilin- und Soda-Fabrik as more suitable than indigo carmine. The end point of the titration is more delicate than with indigo carmine.

Gelatine Solution.—Three grms. of gelatine are dissolved in 100 c.c. of warm water. A drop of clove oil will keep the mixture for a day or two, but it is best to prepare it fresh each time.

Sodium Chloride Solution.—Prepare a saturated solution of sodium chloride and add 50 c.c. of strong sulphuric acid per litre.

The Löwenthal method is of much use where a large number of analyses have to be performed and where comparative results only are required. For example, it serves admirably in the case of spent liquors. It may be further added that as in the hide-powder method of analysis, gallic acid is included with tannins. The method, as originally proposed

by Löwenthal in 1860, has been the subject of many improvements by Procter, Hunt, and others, and the following are the details of the process as now generally used :—

The liquor or extract to be tested is diluted to a suitable strength of from 0·3 to 0·5 per cent. of tannin and filtered through a Schleicher and Schüll No. 605 hard filter paper. Five cubic centimetres of the filtrate are placed in a large porcelain dish with 20 c.c. of indigo carmine solution and 750 c.c. of water, and the permanganate run in till a golden yellow colour tinged at the edges with pink is obtained. The permanganate should be added as far as possible at a perfectly regular rate and slower towards the end of the reaction. At first from one half to one cubic centimetre may be added at once, but as soon as the deep blue of indigo carmine begins to fade the further additions should only consist of a few drops and ultimately be reduced to a single drop. The titration should be repeated at least twice. Fifty cubic centimetres of the filtered liquor are now mixed with 25 c.c. of the gelatine solution in a 100 c.c. flask. Five grms. of washed and powdered kaolin are added, the liquid made up to the mark with the sodium chloride solution, after which it is well mixed and filtered. Ten cubic centimetres (equal to five of the original liquor) are now titrated as before. The permanganate required measures the oxidisable non-tannin bodies included with the tannins in the original titration. Deducting this, we obtain the value in permanganate of the tannins. This correction is necessary, since all tanning substances contain bodies oxidisable by permanganate, but which are not taken up by the hide. The results are calculated into gallo-tannic or tannic acid, but, if preferred, they may be translated into tanning values for the particular material in question, by performing a number of duplicate analyses side by side with the hide-powder method. Instead of using gelatine (Hunt's method) the tanning liquor may be detanned by hide powder, only, of course, it must be remembered that the results of the two methods will not necessarily agree, since the hide powder removes more of the constituents of the liquor than gelatine does, particularly in the case of gallic acid.

Notes on Löwenthal's Method.—Tannins are readily oxidised by permanganate, but other oxidisable bodies are present, and hence the necessity of a second titration to allow for this. The use of saturated salt solution, which was first suggested by Procter, aids the precipitation of tannins and gelatine. The indigo carmine does not merely play the part of an indicator, but prevents the oxidation of the non-tannins present. These bodies are only oxidised somewhat slowly, and in the presence of indigo carmine the latter uses the oxygen which is left over from the oxidation of the tannins, provided the permanganate is not present in a large excess. This is the reason for the regular addition of the permanganate as described.

(12) **The Hide powder Method.**—The unsatisfactory nature of the results obtained by any of the processes already described and dissimilarity to any of the conditions actually obtaining in practice led to the suggestion of the

use of hide as a precipitant or absorbent for tannins and the actual measurement, by differences, of the amount of matter capable of being abstracted from a solution of tannin by this means. In the first experiments pieces of raw hide were used, but these contained much soluble matter, and this is readily increased by putrefaction. Thus raw hide was quickly replaced by a washed, dried, and powdered hide which at first was mixed with the tannin infusion and allowed to stand for some hours and then filtered, the difference between the total soluble matter and the original filtered infusion and that of the detannised filtrate giving the matters absorbed by the hide. The length of time occupied by this process gave rise to difficulties, chiefly owing to the gradual solution of the hide, and suggested to Procter the use of a bell for holding the powder.

As this is the standard method for all purposes a complete description of its adaptation to tanning materials will be given. In the first place, however, before commencing an analysis, considerable care must be paid to the question of sampling. It is, of course, of importance that samples from bulk should be drawn in such a way as to include a fair average, as naturally one bag of smach may in no way represent a bulk lot of 500. Again, in the case of valonia, it is important to see that representative portions of cup and beard are obtained, since the proportion of tannin is much greater in the beard than in the cup. Myrobalans is sometimes badly sampled by forgetting that the poorer and lighter portions will often be found at the top of the bag. Liquid extracts should be thoroughly mixed before sampling, as insoluble matter gravitates to the bottom of the casks. Solid extracts are best sampled by breaking the blocks and rejecting the outside portions. Many solid extracts dry very rapidly when exposed to the air, and samples taken from the surface are not therefore representative. The following are the official regulations of the I.A.L.T.C. for sampling:—

Liquid Extracts.—In drawing samples at least 5 per cent. of the casks must be taken, the numbers being selected as far apart as possible. The heads must be removed and the contents mixed thoroughly by means of a suitable plunger, care being taken that any sediment adhering to sides or bottom shall be thoroughly stirred in. All samples must be drawn in the presence of a responsible person.

Gambier and Pasty Extracts.—Gambier and pasty extracts should be sampled from not less than 5 per cent. of blocks, by a tubular sampling tool, which shall be passed completely through the block in seven places. Solid extracts shall be broken, and a sufficient number of portions drawn from the inner and outer parts of the blocks to fairly represent the bulk. In both cases samples shall be rapidly mixed and enclosed at once in an air-tight bottle or box, sealed and labelled.

Valonia, Algarobilla, Divi-divi and General Tanning Materials.—Valonia, algarobilla, and all other tanning materials containing dust or fibre shall be sampled, if possible, by spreading at least 5 per cent. of the

bags in layers one above another on a smooth floor, and taking several samples vertically down to the floor. Where this cannot be done the samples must be drawn from the centre of a sufficient number of bags. While valonia and most materials may be sent to the chemist ground, it is preferable that divi-divi, algarobilla, and other fibrous materials shall be unground. Bark in long rind and other materials in bundles shall be sampled by cutting a small section from the middle of 3 per cent. of the bundles with a saw.

Samples for more than one Chemist.—Samples to be submitted to more than one chemist must be drawn as one sample, and well mixed; then divided into the requisite number of portions not less than three, and at once enclosed in suitable packages, sealed and labelled.

Preparation for analysis. The following regulations require no comment:—

Quantity of Material to be taken for Analysis.—The quantity taken should be such that the solution shall contain from 0.35 to 0.45 grm. per 100 c.c. of tannin matter absorbed by hide. Liquid extracts must be washed into a covered beaker or basin, from which they are washed into a litre flask with boiling water and well shaken, the flask being finally filled to the mark with boiling water. The neck is then covered with a small beaker and a flask placed under a cold water tap and rapidly cooled to the temperature of 15° C. The volume is then made up and the solution thoroughly mixed.

Solid Extracts are dissolved by stirring in a beaker with boiling water, the undissolved portions being allowed to settle and treated with further quantities of boiling water and the solution poured into a litre flask. When the whole of the extract has been dissolved or washed into the flask it is cooled as above.

The following weights of tanning materials are given by Paessler (*Collegium*, 1904, 84), which will give the requisite strength of solution, 3.5–4.0 grms. of tannin per litre:—

TABLE XXXA.

	Grms.		Grms.
Algarobilla,	9	Mangrove bark,	10
Canaigre,	18	Mimosa bark,	12
Divi-divi,	9	Myrobalans,	12
Oak bark,	36	Quebracho wood,	22
Oak wood,	50	Rove and other galls,	12
Pine bark,	32	Sumach,	16
Garouille,	16	Trillo,	10
Hemlock bark,	32	Valonia,	14
Chestnut wood,	45	Willow bark,	36
Knoppem,	12	Used materials,	50

Solid extracts, 5–7 grms.

Pasty extracts, sp. gr. above 1.2 or 25° B_é, 9–12 grms.

Liquid extracts, sp. gr. above 1.15, or 19° B_é, 12–18 grms.

Liquid extracts, sp. gr. below 1.15, or 19° B_é, 18–20 grms.

In making up solutions of extracts for analysis it is important to remember that in many cases, such as valonia, quebracho, etc., the amount of insoluble matter or difficultly soluble tannins is affected by the strength of the solution. Thus while a dilute solution may be perfectly clear, a somewhat stronger one will contain a considerable amount of undissolved matter. A solution made with cold water will also often give a different result to one made by digestion on the water-bath at a temperature of 60° to 80° C. Finally, an extract cooled very slowly will give more insoluble matter than one cooled rapidly in a stream of cold water. Hence it is necessary to observe rigid conditions in making up these solutions to obtain concordant results.

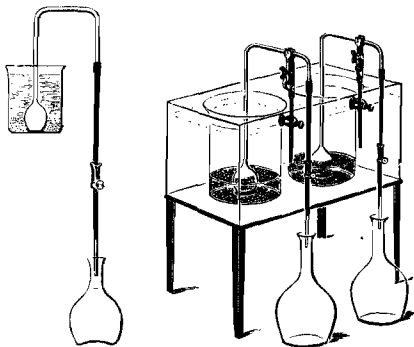


FIG. 21.

Solid tanning materials, barks, etc., must be finely ground till the powder will pass through a sieve of five wires per centimetre. In the case of bodies that cannot be ground the sample must be separated by means of a sieve into coarse and fine portions. Each of these is then weighed and proportional parts taken for analysis. The requisite quantity of the powder is then weighed out and extracted by the method described below.

Extraction of Solid Tanning Materials for Analysis.—A beaker of about 500 c.c. capacity, preferably of porcelain, is placed in the water-bath, as shown in fig. 21.

A thistle-headed funnel, the stem of which is bent twice at right angles, and of which the head is covered by a piece of fine silk gauze to act as a strainer, is placed in the beaker and held in position by means of a clamp. A piece of glass tube is attached to the free end of the stem

by means of indiarubber tubing, provided with a screw clamp by means of which the flow can be regulated. Fine silver sand is now poured into the beaker, so as to surround the head of the funnel to about half an inch in depth.

Since the sand often contains iron and other soluble matter it must be washed by hydrochloric acid and then thoroughly with water, while should it contain grease, ignition is necessary. The weighed quantity of tanning materials is then introduced, the beaker filled with water and allowed to stand overnight. In case of urgency water of 30° to 50° may be used and the extraction proceeded with after the material is thoroughly soaked.

Percolation is started by sucking the syphon and allowing the liquid to drop slowly into a litre flask, the water-bath being maintained at a temperature of from 30° to 50° C. until about 400–500 c.c. of the liquid has come over, after which the temperature may gradually be raised to boiling point.

If the liquid in the syphon is not colourless after about 750 c.c. have been drawn over, commence collecting the following portions in a separate flask and proceed until the extract gives no turbidity with hide-powder extract. At this stage the liquor in the syphon is practically colourless. Concentrate the contents of the second flask if necessary, add to the original extract and make up to 1000 c.c. Concentration is, however, rarely necessary. At the Turin Conference, September 1904, Procter stated that all the tannins could be got out with a litre of water, and what was afterwards extracted was useless from the tanner's standpoint, as it was so difficultly soluble. It is now usual to complete the extraction in 2½ to 3 hours and neglect all that subsequently comes over.

Preservation of Extracts.—If not analysed at once, extracts should be preserved by means of a drop of oil of clove or mustard.

Other Methods of Extraction of Materials for Analysis.—The simplest method of extracting tanning materials is to boil them with water under an inverted condenser and then to decant the solution through a filter, repeating the process with several successive quantities of water until the washings are quite colourless and give no qualitative test for tannin. Where time is a matter of importance, and especially when comparative numbers only are required, this method is perfectly legitimate, though the results finally obtained will, as a rule, be somewhat low for the following reasons:—

- (a) It is found that most tanning materials have a maximum temperature of extraction.
- (b) Solutions of tannin are gradually decomposed by boiling, especially in the presence of air.

The method now universally adopted for the extraction of tanning materials is the sand-filter method, first used by Professor Procter, and described above. Many other forms of extractors have been suggested and employed, of which the following are the more important:—

The Weiss Extractor.—This consists of a metal Soxhlet in which the material is placed and subjected to continuous extraction with boiling water. The chief objection to its use is the continued boiling and periodic concentration of the solution in the receiver, which undoubtedly leads to some loss of tannic acid. This loss can, however, be minimised by withdrawing the solution frequently and replacing it with fresh water. This procedure, however, introduces a fresh objection, namely, that a very large volume of water is sometimes to be employed in order to obtain complete extraction, and necessitating subsequent concentration before analysis. In spite of these objections the process has been proved to extract more than the sand percolating filter, and particularly so in the case of barks which, on account of their bulkiness, are very difficult to properly extract by the official process.

The Koch Bottle-Extractor.—This apparatus consists of a wide-necked bottle of thin, well-annealed glass holding about 200 c.c. The bottle is fitted with a two-hole rubber bung through which pass two tubes, a short one just projecting below the bung and a longer one reaching to the bottom of the bottle and widened to a funnel at its end. The latter is covered with silk gauze, such as millers use, and sunk in a layer of pure sand 2 centimetres thick. Above the sand is introduced a weighed quantity of ground tanning material. Both tubes bend at right angles above the bung, and are connected, the shorter with a water-supply 1½ metres above the bottle, the larger with a litre flask, the rubber connection in each case being fitted with a screw clip to regulate the inflow of water and the outflow of tanning extract. The bottle with its bung secured by wire on a special clamp is immersed in a water-bath kept at the desired temperature.

The Veitch Extractor.—P. Veitch (*Collegium*, 1905, p. 291, and 1906, p. 250) describes a form of continuous extractor which does away with prolonged boiling and repeated concentration and dilution of the solvent, and the results of a large number of parallel experiments conducted with this and other forms of apparatus show that complete and quick extraction is readily obtained. The extractor (fig. 22) is made of glass or copper in the form of a double tube or side tube extractor, as devised by Zullkowsky. The material to be extracted is ground and mixed with water to a thin paste. It is then placed on a perforated porcelain plate resting on the bottom of the extractor and pressed down firmly. Any cloudy extract which passes into the receiving

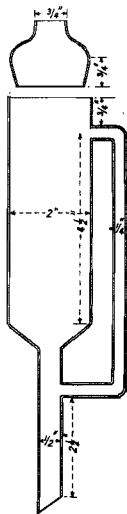


FIG. 22.

flask is returned to the extractor and another perforated plate is placed on the top of the mass in order to keep it compact and distribute the condensed water. The end of the condenser is placed below the level of the side tube so as to prevent the upper disc from rising above this point. Undue concentration is avoided by placing 250 c.c. of water in the receiver

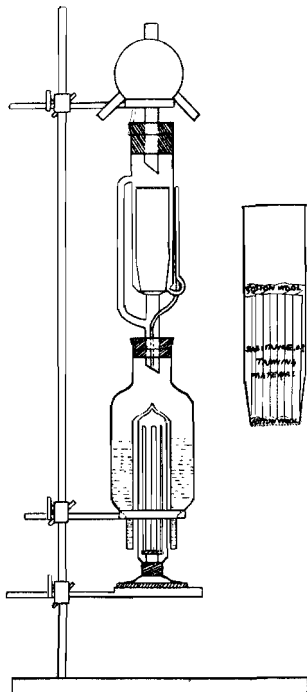


FIG. 23.

and changing it after a short time for a second and third similar quantity, the whole extraction being completed with 1 litre. In the case of bodies requiring partial extraction at low temperatures, water at the necessary temperature is poured by degrees into the extractor, allowing each lot to run through before the next addition. When sufficient has been collected at this temperature water is placed in the receiver and the extraction completed as usual. Veitch found that for the same time of extraction his method gave higher results than those of Koch and Weiss. In some cases in which from 3 to 6 litres of extract had been obtained by this method the Weiss continuous extractor still gave an extract containing a considerable amount of tannin. Veitch and Hurt (*Collegium*, 1906, p. 250) give a series of figures which seem to show that complete extraction of tanning materials can only really be obtained by some form of condenser or

Soxhlet extractor, and they conclude that a Soxhlet which does not require too great a concentration of the liquor between the syphonings will always give complete extraction, especially if undue concentration be prevented by

the removal of the liquor and its replacement by water in the first few syphonings. In the case of sumach and cauaigre, where with the official method a considerable volume is collected at a comparatively low temperature, Veitch collected only 250 c.c. at the lower temperature and then completed the extraction at steam heat and found the results to be better than those obtained by other methods.

Extraction with Organic Solvents.—Alcohol, acetone and other solvents have been proposed, but have generally been objected to chiefly on account of the probable presence of resins and partly because certain glucosides do not dissolve so readily in alcohol as in water. Experiments made in the author's laboratory (Trotman and Hackford, *J.S.C.I.*, 1905, 1099) seem to show that the results obtained by alcoholic extraction in the case of many materials agree with those of aqueous extraction, while much time is undoubtedly saved. That hydrolysis does not take place was proved by boiling a sample of lentisco extract for a long time with alcohol, after which the results obtained by analysis were found to be identical with those obtained before. The following special form of apparatus was used (fig. 23):—

The alcohol is placed in a flask with a re-entering bottom, in which is fitted a cylindrical electric lamp, the filaments of which are similar to those employed in electric radiators. The lamp is raised or lowered as may be necessary. The extraction will be complete when the spirit comes from the Soxhlet extractor colourless, and generally does not require more than half an hour. Table XXXI. (*loc. cit.*) shows the percentage of total solids obtained by the two methods.

TABLE XXXI.

	Total solids by Procter's method.	Total solids by Trotman and Hackford's method.
Sumach,	30·68	31·40
Lentisco,	30·00	30·01
Larch,	15·46	16·40
Birch,	13·77	13·05
Gambier,	81·44	79·20
Cutch,	42·48	46·82
Divi Divi,	50·72	58·42
Myrobalans, . . .	50·72	54·36
Tamarix,	26·24

The following figures show that, for sumach at any rate, the use of alcohol as a solvent would be permissible, and the process being rapid makes a very good check upon the I.A.L.T.C. method.

TABLE XXXII.

Sumach.	Total soluble matter I. A. L. T. C. method.	Total soluble matter extracted with alcohol.
1	43·84	42·28
2	51·20	52·80
3	42·08	41·90
4	30·68	31·40
5	45·36	44·94

With some other materials the results do not agree so well.

Filtration of Extracts for Analysis.—After the extraction has been completed, the liquid is rapidly cooled by a stream of cold water, made up to the mark and thoroughly mixed. If more than a litre has been collected the first 700 or 750 cubic centimetres are set aside and the remainder collected in a separate flask. A funnel is placed in the neck of the flask and the contents boiled rapidly over a naked flame till its volume is less than 250 c.c. It is then poured into the first flask and the whole cooled, made up to a litre and mixed.

Before beginning the analysis it is necessary to obtain a perfectly bright filtrate, no opalescence or turbidity being permissible. Two methods of filtration may be used, the latter of which is the official one, the former being only made use of where it is impossible to obtain a satisfactory filtrate by the official method. They are—

(a) Filtration through specially prepared filter paper.

(b) Filtration through a porcelain candle filter.

(a) *Filtration through Paper.*—Until recently this was the official process. A specially hardened ribbed paper of about 13 cm. diameter (Schleicher and Schüll No. 605) is placed in a funnel and filled with the liquid. If the filtrate is not perfectly clear it must be returned to the filter. Sometimes, especially with solutions of solid extracts, it is extremely difficult to obtain a clear filtrate. In this case some washed and ignited kaolin is washed with some of the extract and then mixed with the remainder and poured into the filter, returning the filtrate till perfectly bright and clear. From 150 to 200 c.c. of the filtrate are now collected and set aside, after which the next 100 c.c. are used for the determination of the total solids. There are some difficulties in connection with the use of filter paper with tanning solutions, chiefly owing to the fact that it has itself a certain capacity for absorbing tannin and other substances from the solution, this capacity varying with the nature of the paper and of the tanning solution. It is also affected by the speed of filtration (Farker and Payne, *Collegium*, 1904, 249). By rejecting the first 200 c.c. it was thought that the errors due to absorption would be eliminated, but experiments, chiefly by Procter and Blockley, proved that this was not the case and that it

sometimes required the passage of nearly a litre of liquid to saturate the paper, the volume as pointed out by Parker depending obviously upon the rate of filtration. Procter and Blockley (*J.S.C.I.*, 1903, 765), as the result of numerous experiments, found that if 150 c.c. were rejected and the following additions (Table XXXIII.) made to the weights of the total solids a truer result was obtained. Their experiments were also extended to include certain other papers then in use. Of these Dreverhoff's No. 311 is recommended by some chemists on account of its comparative cheapness, while Schleicher and Schüll No. 590 is also frequently used.

TABLE XXXIII.

Filter Paper.	Tanning Material.	Correction in Mgrms. for 50 c.c. of liquor.
Schleicher and Schüll's 605,	Oakwood extract.	5.0, 5.5, 5.3, 3.3, 4.5, 4.5.
" " "	Sumach.	5.5, 5.7, 6.1.
" " "	Chestnut extract.	5.0, 4.5, 3.5.
" " "	Oak bark.	7.1.
" " "	Mimosa bark.	5.3, 5.5.
" " "	Mimosa extract.	6.4.
S. and S.'s 590,	Various.	1.0 (average).
S. and S.'s 590 + kaolin (A.O.A.C. method; <i>J.S.C.I.</i> , 1903, 130).	"	5.0 (average).
S. and S.'s 605 + kaolin,	Solid Quebracho extract.	7.8, 9.2.
Dreverhoff's 311 + kaolin,	Oakwood extract.	5.5, 3.0.
" " "	Chestnut extract.	5.0.
" " "	Sumach extract.	4.3.

Further experience proved that even with the corrections concordant results were not always assured, for it was impossible to guarantee that different batches of the same paper were of exactly the same composition and had identical coefficients of absorption. Hence it is preferable to check the correction occasionally.

(b) The American method of filtering (A.O.A.C. and *J.S.C.I.*, 1905, p. 130) is as follows:—

Single pleated Schleicher and Schüll No. 590 papers, 15 cm. in diameter, are used. Seventy-five c.c. of the tannin solution are stirred with 2 grms. of kaolin, and, after standing for 15 minutes, as much as possible of the liquid is decanted off and another 75 c.c. of the tannin solution added. After stirring and standing for 15 minutes, this is decanted on to the filter, which is then filled up with the liquor. The first 150 c.c. are rejected. Evaporation during filtration must be guarded against.

(c) *The Candle Filter*.—In order to overcome the difficulties connected with the use of filter papers, Parker and Payne (*Collegium*, 1904, p. 249) made experiments with various filtering media, such as kaolin, kieselguhr, sand, asbestos, and glass wool, and, ultimately, with filter candles, such as are used for filtering bacterial and other liquids; they finally adopted a

Berkefeld filter candle which, with slight modifications, has been adopted as the official filter by the I.A.L.T.C. The candle is 7 centimetres in length and 3 in diameter. Having been freed from iron salts and other soluble matter by digesting in a 50 per cent. solution of warm hydrochloric acid, it is thoroughly washed with distilled water and dried. The candle (K) is then mounted in a thistle funnel (B), a rubber band (A) being placed round the bottom of the funnel to connect it with the thistle funnel shown in fig. 24. This thistle funnel is then

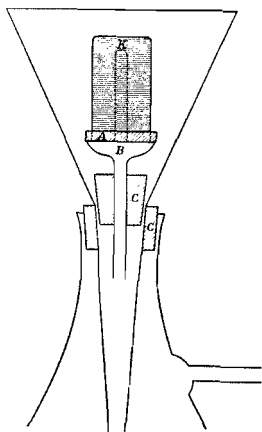


FIG. 24.

passed through a rubber bung which fits into a large filter funnel placed in the neck of an Erlenmeyer filter flask connected with a vacuum pump, a trap being provided between the pump and the flask. The funnel is now filled with the liquid and a vacuum of about 40 millimetres obtained, when the rubber tube connecting the flask to the pump is closed by a screw clamp and a glass plate placed over the top of the funnel to prevent evaporation of the liquid. In about a quarter to half an hour sufficient filtrate will be obtained. As the vacuum in the flask is gradually reduced by the incoming liquid the water vapour re-condenses and thus minimises the loss by evaporation. In the case of liquors which are difficult to filter the candle may be occasionally brushed with a hard tooth-brush which has been previously steeped in the liquor. Some-

times it is difficult to obtain a perfectly clear extraction, especially with gambier and sumach, the first filtrate being distinctly turbid. In such cases the solution must be passed through the filter again with, if necessary, the addition of a little kaolin until it is perfectly clear. In some instances it will be found easier to obtain a satisfactory filtrate with the paper. If this method is resorted to the fact should be stated upon the report. After the candle has been used it should be cleaned by carefully washing the surface and passing a quantity of water or dilute hydrochloric acid through it; and before being used again it must be thoroughly dried.

Analysis of the Filtered Extract.—This consists of two operations—

- (1) Determination of total soluble matter.
- (2) Determination of soluble non-tannins.

These figures, together with the percentage of moisture and ash determined on the original sample, give all the information that is usually required. Special materials sometimes require other tests for the detection of specific adulteration, but these will be referred to later.

Determination of Moisture.—The moisture is determined by drying a suitable quantity at the temperature used for the determination of total soluble matter. In the case of extracts giving turbid solutions which cannot be thoroughly mixed, after mixing the solution and before filtration measure off and evaporate 50 c.c. in the same way as in total soluble matter.

Determination of Ash.—A weighed quantity of the material is ignited in a platinum dish in a muffle furnace or over a bunsen burner, the ash in most cases being grey or white, although in the presence of much iron it will be brown. The total ash having been determined, it is treated with strong hydrochloric acid, the insoluble silica filtered off, washed, ignited, and weighed. If iron be present, the filtrate is made up to known volume and an aliquot portion of it tested by means of free potassium ferrocyanide or sulphate cyanide in the same way as described in water analysis.

Insoluble Matter.—If the sum of the tannins and non-tannins be deducted from 100 parts of the dry matter the difference represents insoluble matter.

The statement of analysis is usually made in the following way:—

(1) Tanning matter absorbed by hide. Obtained by deducting the "soluble non-tanning matter," found by evaporating the hide-powder filtrate, from the "total soluble."

(2) Soluble non-tanning matters. Found by evaporation of filtrate from hide-powder filter.

(3) Insoluble matter. The difference between "total soluble matter" and the "total dry matter."

(4) Moisture. Determined by drying a portion at the temperature adopted in the determination of "total soluble."

(1) **Total Soluble Matter.**—Two separate portions of 50 cubic centimetres of the clear filtrate obtained as described above are evaporated on the water-bath in a suitable nickel or platinum dish, and dried in an air-oven at 100° C.—105° C. till constant in weight, and the residues weighed. Nickel dishes are very suitable for these determinations. Schweitzer (*Collegium*, 1904, 23) recommends the use of a flat dish with a cover, which is put on while weighing. The same author advises the use of a vacuum drying oven, and considers that a temperature of 105° C. is somewhat too high for many tannin residues, and prefers drying at a lower temperature with the increased rapidity obtainable by means of a partial vacuum. A convenient and simple form of laboratory vacuum oven may be made by fitting a bell-jar with a rubber bung through which passes an electric wire (fig. 25) from the main supply, connected internally with a lamp. Through a second hole in the bung passes a tube connected with a vacuum

pump, a screw clamp being provided to close the tube when a sufficient vacuum is obtained. The dish containing the residue is placed on a small tripod stand on the floor of the oven, the lamp being near the top. With a 16-candle-power lamp it is perfectly easy to maintain a constant temperature of about 60° C. within the jar.

(2) **Determination of the Soluble Non-tannins.**—This consists in the removal of the tannins from the solution and re-determining the remaining soluble matter by evaporation of a measured quantity. There are several

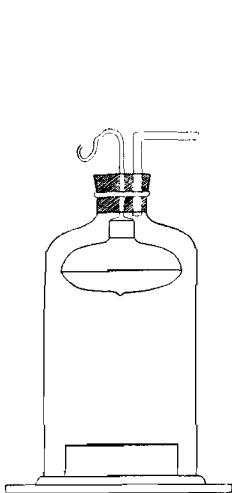


FIG. 25.

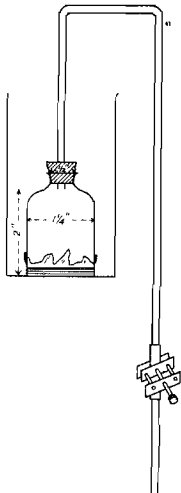


FIG. 26.

processes which may be used for this purpose, but only a few call for special description, viz., those in which hide powder is employed, and of these the following are or have been officially recognised:—

- (1) Procter's bell-filter method.
- (2) The American shake method.
- (3) The Palmer method.
- (4) The chromed hide powder method.

The Bell-filter Method was first described by Procter, and with certain modifications was, until quite recently, the official process of the I.A.L.T.C. It is carried out as follows:—

A glass bell open at both ends (fig. 26) is fitted with an indiarubber cork through which passes a narrow syphon tube. The top of the bell is plugged with a piece of cotton or glass wool, and the bell filled with 6.5 to 7.5 grms. of hide powder, which should be carefully packed so that no channels are left and that the rate of flow through the syphon should be about 1 drop in 2 seconds. After inserting the cork and syphon, a piece of muslin is then tied over the bottom of the bell, which is now placed in a small beaker somewhat higher than the bell.

The standard filter bell has the following dimensions: length, 7 cm.; diameter of neck, 1.8 cm.; diameter of end, 3 cm. As a matter of fact a bell of these dimensions is very difficult to work with, the height being too great and the diameter too little. More satisfactory bells may be obtained with the following measurements: length, 2 ins.; diameter of neck, $\frac{1}{2}$ in.; diameter of end, $1\frac{1}{4}$ in.

Since all hide powder contains some soluble gelatinoid matter, the first runnings are collected separately till this has been removed. As a general rule, if the packing has been properly carried out, all the soluble matter will be removed when 30 cubic centimetres have been collected. The freedom from gelatine is ascertained by allowing a few drops from the syphon to fall into a little filtered cold-water extract of hide powder, or a little collin solution. In the presence of gelatine a turbidity will be observed. In this case the filtrate must be tested every few minutes till no reaction is produced. If after 30 c.c. have been collected the filtrate is free from gelatine, the next 60 c.c. are collected in a separate cylinder. This portion should be free from both soluble matter and tannic acid. Freedom from the latter body may be tested by allowing the next few drops to fall into the cylinder containing the first portion of the filtrate, or, if preferred, into a little cold extract of hide powder or collin solution. If no turbidity is produced, the filtrate may be used for the determination of the soluble non-tannins, by evaporating 50 c.c. of it in a weighed nickel dish on the water-bath, and drying at 100° C.—105° C. till constant in weight. From the weight of the residue the percentage of soluble non-tannins may be calculated, and the difference between the weights of total soluble matter and soluble non-tannins gives the tannins absorbed by the hide powder. The following example will make this clear:—

Weight of sumach taken	=	10 grms.
Extract made up to 1000 c.c.		
(a) Total solids from 50 c.c. weighed		0.2315 grm.
(b) Soluble non-tannins ,, ,,		0.0800 ,,
∴ Tanning matter absorbed by hide in 50 c.c. extract	=	0.1515 ,,
∴ 10 grms. sumach gave		3.030 ,,
	=	30.30 per cent.

An automatic form of bell-filter has some advantages, and may be made as follows (Earp, *Collegium*, 1903, 275):—

The lower end of the syphon filter (fig. 27) is passed through one hole of a two-holed cork, which fits closely into a graduated cylinder of about

60 c.c. capacity. Through the other hole passes a glass tube about 15 inches long, open at both ends, and capable of sliding up and down through the cork. The other limb of the syphon is attached to the bell containing

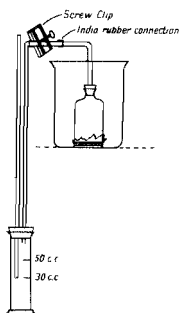


FIG. 27.

the hide powder. The lower end of the sliding tube is adjusted to coincide with the 30 c.c. graduation of the cylinder, the liquid having been drawn over by suction at the upper end. The filtration goes on until the 30 c.c. mark is reached, when the liquid ascends in the sliding tube, stopping when the levels of the liquid in the tube and in the bottle are the same. The graduated jar is then emptied and the sliding tube adjusted to the 50 c.c. mark, and the filtration continued.

Certain tanning materials, such as man-grove and cutch, cannot always be fully detannised under the official conditions unless a weaker liquor is employed. When this is found necessary the fact should be stated. It is important that the extracts should be analysed on the day of their preparation, since, if allowed to stand for any length of time, they gradually undergo decomposition, accompanied by decrease of tannins, and often by increase of non-tannins; further, if the rate of filtration during detannisation be unduly slow, uncertain results will be obtained. The following experiments of Nihoul (*Bull. de l'Assoc. belge de Chim.*) illustrate this point. Experiments were made in the two directions briefly indicated.

(a) *Interaction between Soluble Non-tannins and Raw Hide when Oxidation is limited.*—"Non-tannin" solutions were prepared exactly as in analysis by the I.A.L.T.C. method and mixed with uncoloured hide powder from the upper portion of the bell-filter after analysis, i.e. powder saturated with detannised liquor.

Small flasks were filled to the brim with these mixtures of soluble non-tannins and hide powder, a trace of thymol added as a preservative, and they were set aside for periods of one, three, and five weeks. The mixtures were then filtered, and the soluble non-tannins determined by evaporation just as in analysis, the results being incorporated with the analysis made at the beginning of the experiments, just as if no delay had occurred.

It appeared that the non-tannins of chestnut are increased, and they exert a solvent action on the hide powder, while the non-tannins of pine bark and sumach are diminished, and would therefore give better results in the tanyard than an analysis by the present method indicates.

(b) *Behaviour of Non-tannin Solution exposed to Air.*—Small flasks were filled with clear non-tannin solution preserved as before by thymol, but

containing no hide powder in suspension, and allowed to stand for 14 to 64 days. After 14 days portions were passed through the hide filter, to determine whether any of the non-tannins had changed into tannins, *i.e.* matter absorbed by the hide. In the case of chestnut and pine the original amount of tannin was increased by nearly 1 unit per cent. and by nearly 4 units in the case of sumach. After 64 days the liquors had all formed precipitates. They were filtered, and a portion of each evaporated to find the change in the amount of non-tannins. Another portion was passed through the hide filter, to find whether the whole was still non-assimilable. It was found that little more than 50 per cent. of the original soluble non-tannins now passed through the filter.

In the above description of the bell-filter method it is assumed that the whole of the soluble matter will be removed by the first portion of the filtrate, but in practice this is rarely the case, and generally an allowance has to be made for soluble matters not so removed. Each fresh batch of hide powder must be tested with distilled water in exactly the same way as it is used with the tanning solution, rejecting the first 30 c.c. of the filtrate and evaporating the next 50 c.c. and weighing the residue. The weight of this residue must be deducted from the weight of soluble non-tannin found in the above analysis. A hide powder which is kept for any length of time must be carefully preserved from air, and it is further advisable to retest it with distilled water from time to time. When kept, especially if damp, it undergoes decomposition, probably of the nature of hydrolysis, which causes an increase in the soluble matter.

TABLE XXXIV.

	Factor of solubility for 50 c.c. 0.039 grm.		Factor of solubility for 50 c.c. 0.1725 grm.	
	Tannins.	Non-Tannins.	Tannins.	Non-Tannins.
Oak Wood Extract, .	25.20	20.00	34.80	10.20
Quebracho Extract, .	70.30	14.30	79.30	5.60
Quebracho Wood, .	18.20	1.80	22.50	1.50
Valonia, .	23.30	15.10	31.00	7.30
Pine Bark, .	13.10	9.00	17.40	3.10
Mimosa Bark, .	36.80	11.60	44.80	5.10

The effect of excessive moisture on hide powder has been investigated by Turnbull (*Leather Trades Review*, xxxiv. [785], 226), who tested an ordinary dry powder and then retested it at intervals, allowing it to absorb moisture from the air. He found that the matters soluble in water gradually rose as shown, 25 c.c. of the first 30 giving in April a residue of 0.0113 grm. as against 0.0186 in June. Table XXXIV. (*Maschke, J.S.C.I.*, 1898, 879) shows the difference in the results in estimations of

tanning matter, when the tannins are absorbed by (1) hide powder of good quality, and (2) hide powder of indifferent quality.

In the first case the factor of solubility was 0.039 grm. per 50 c.c. filtrate, and in the second 0.1725 grm.

A good hide powder should be white, soft and woolly, and before use must be tested with distilled water in exactly the same way as in the analysis of a tannin liquor, and must fulfil the following requirements¹ :—

1. The percentage of nitrogen must not be less than 11.5 calculated on a basis of 18 per cent. of moisture.

2. Pure cellulose may be added to the extent of 10 to 20 per cent. :

3. The amount of soluble hide substance in the test with distilled water must not exceed 5 milligrammes per 50 c.c.

4. The non-tannin filtrate must not give a turbidity with a salt gelatine solution made as follows :—

Two to three grms. of gelatine and 100 grms. of sodium chloride are dissolved in 500 c.c. of water, cooled to 28° C. and filtered. The reagent is used in the proportion of 1 drop per 5 c.c.

Gordon Parker (*Collegium*, 1904, 184) states that poor hide powder may often be improved in quality by rejecting that portion of it which will pass through a sieve of 40 meshes per linear inch.

Cellulose in hide powder is readily detected by Kopecky's test (*J.S.C.I.*, 1905, 639). From 0.2 to 0.3 grm. of the powder is moistened with a solution made by adding extracts of potassium iodide to 100 parts of zinc chloride solution (sp. gr. 1.8), and saturating the solution with iodine. After allowing the mixture to stand for 2 or 3 minutes 25 c.c. of water are added and the pulpy mass well stirred. The cellulose particles are coloured a deep violet and can easily be distinguished from the hide, which becomes yellow.

It is sometimes impossible to obtain hide powder which will satisfy the requirements, and at times it is therefore necessary to use one which should really be rejected. This difficulty may be got over by the following method (Trotman and Hackford, *Collegium*, 1905, 359) :—

Five grms. of hide powder are placed in a mortar and ground for about 5 minutes with 50 c.c. of the tannin liquor, in order to remove the soluble matter. The last traces are eliminated by pouring the contents of the mortar into a funnel of the Gooch crucible type, filtering off the liquor and washing with a small quantity of the liquor. The hide powder is then freed from the filtrate by pumping and pressing with a spatula.

About a third of the prepared hide powder is then taken, and stirred by means of a small mechanical stirrer, with 150 c.c. of the liquor to be detannised. The stirring operation lasts for 5 or 10 minutes, at the end of which time the solution should be colourless, indicating that the greater part of the tannin acid has been removed.

While the stirring operation is in progress the remaining two-thirds of

¹ *Collegium*, 1902, 327.

the prepared hide powder are ground in a mortar with 100 grms. of silver sand, the object being to increase the available surface of the hide powder, and further to make a medium in which channels shall be less apt to form than in the hide powder itself.

The contents of the mortar are now transferred to a Gooch funnel of about 2-in. diameter, in which a mat of asbestos has been placed and pressed dry.

The 150 c.c. of partially detannised liquor are now passed through this filter of sand and hide powder, and thus the last traces of tanning materials are removed. The flow of the filtrate is controlled by means of the pump. The first 20 c.c. are rejected, and of the remainder 50 c.c. are evaporated to dryness and weighed as usual.

The following figures were obtained in the author's laboratory, showing the difference in the soluble non-tannins as estimated by his and Procter's method:—

TABLE XXXV.

	Wt. of S.N.T. when filtered in usual manner.	Wt. of S.N.T. when filtered slowly.	Wt. when filtered by Trotman and Hackford's method.
1	·0710 grm.	·0800	·0640
2	·0714	·0816	·0700
3	·1828	...	·1172
4	·0731	...	·0716
5	·1121	...	·1160
6	·0240	...	·0208

From the above experiments the consistency of the results obtained is shown. If in Procter's bell method ·02 is allowed as correction for soluble hide powder, such a substance as sumach, in which 10 grms. are used in analysis, has its results influenced to the extent of 2 per cent., while quebracho extract, in which only 3 grms. are taken, this correction figure affects the results to an extent of 10 per cent. If the soluble non-tannins are filtered slowly the correction is still greater, as shown in examples 1 and 2. This is without doubt one of the facts which cause the divergence of results obtained by different chemists.

The consistency of the results obtained no doubt depends upon the elimination of this error. That the method actually does remove the last traces is shown by the fact that in every case the figure given is less than that given by the bell-filter.

The method indicated in the paper for detannising the liquors was found to be very useful at a time when there was much difficulty in getting a hide powder that would comply with the I.A.L.T.C. requirements, the soluble matter being entirely washed away and hence allowing of the use of a somewhat inferior substance. But such complete detannisa-

tion is not always desirable, the lowest results obtained for the soluble non-tannins not always being the most accurate.

Preparation of Hide Powder.—A fresh ox-hide is well soaked and washed in order to free it from blood and dirt, after which it is limed for about a week, fleshed and unhaired, and cut up into pieces about 1 in. square. After treatment with a 1 per cent. solution of pure hydrochloric acid it is thoroughly washed until chlorides fail to be detected. The pieces are then collected, placed on a clean material, such as linen, and dried as rapidly as possible in a current of cold air, the temperature being raised at the finish to about 40° C. It is then ground in a suitable mill. Cerych recommends that the hide powder should be mixed with paper pulp.

Criticisms of the Bell-Filter Method.—Although the bell-filter method marked a great advance on the methods previously employed, it was always recognised as being imperfect and has been subjected to great criticism, which gradually increased in volume as prolonged experience revealed its defects. The cumulative results of these criticisms has led to its recent abandonment as the official method of the I.A.L.T.C. Under these circumstances it is only necessary to refer briefly to some of these defects, which are, however, very quickly found by those who have to use the method. At the outset one is met with the great difficulty in obtaining a satisfactory and regular supply of hide powder. One is often bound to use a specimen that should be unhesitatingly rejected simply because no better is available. Even supposing this difficulty to be overcome, the packing of the filter bell is by no means an easy matter, and bad packing invariably gives misleading results and causes waste of time and material.

If too loosely packed the liquid will form channels through the powder, and will consequently not be completely detannised, while if too tightly packed the swelling of the powder will make it almost impervious, and the filtrate will only come over very slowly or not at all; and if the filtration be too slow the soluble non-tannins will generally be too high. Further, some hide powders swell much more than others, and all are affected by acid if present in the liquors.

The difficulty in removing soluble matter has already been referred to. If the powder has been carelessly prepared or made from unsound hides, no amount of washing will completely remove the soluble matter, while it possesses at the same time an abnormal power of absorbing colouring matters and other constituents from the liquors during analysis. All hide powders, in fact, absorb considerable amounts of soluble non-tannins and colouring matters, so that the soluble non-tannins are very often too low. Thus gallic acid is absorbed, and hence co-estimated with tannic acid. Exhaustive experiments on the absorption of non-tannins by hide powder have been made by Procter and others, all of whom conclude that the error introduced is a serious one, and one which is rendered more acute by reason of the fact that the nature of the non-tannins is largely unknown. The solution of non-tannins is aided by the fact that the liquid is detannised by the

lower layers of powder in the bell, so that the upper portions of the powder are always in contact with a detannised solution. This indicates one difficulty of the method, namely, that excess of hide powder is always present, while in tanning operations there is always excess of tannic acid.

Effect of Acid.—Among non-tannins, acids, such as lactic, often cause difficulties. In the first place, if present, the non-tannin and total soluble residues should be dissolved in water and titrated with decinormal soda and phenolphthalein, and allowances made for the quantities found. If acids be present in any considerable quantity, they will further cause the hide powder to swell so much that filtration is impossible. On the other hand, certain extracts cannot be properly detannised by neutral hide powders. Many attempts have been made to prevent the absorption of non-tannin and to overcome the difficulties caused by acids by the addition of certain substances or acids to the extract or powder, but these have all been unsuccessful. A further difficulty, connected either with the presence of acid or the method of packing the bell, is that the rate of flow, as already mentioned, seriously affects the weight of the non-tannins. Thus, as shown in Table XXXV., a filtrate obtained at the usual rate gave a residue of 0.0714 grm., while when filtered slowly it was 0.0816 grm. Having regard to the fact that, owing to multiplication, small differences in the weights of the residues exercise a considerable effect upon the results, these divergences become matters of importance.

Almost innumerable attempts have been made to evolve a method of detannising the solution which is free from these objections, and they may be divided into two classes, namely:—

- (1) Those which have for their object the use of an improved powder, notably chromed hide powder, or are conducted with ordinary hide powder under modified conditions.
- (2) Those which attempt to detannise by other agents than hide powder.

Among the former methods are the shake method with ordinary hide powder, the Palmer method, and finally various methods which have led up to the official chromed hide powder process.

The attempts to dispense with hide powder have generally been founded upon the scientific basis that a proper method of tannin determination should consist in the precipitation of an exact compound of tannic acid which is capable of being weighed or otherwise estimated. Among these may be mentioned the attempts to precipitate with alkaloidal or other bases, and perhaps the Collins method of Parker and Payne.

As some of these processes are of considerable value, they may be more particularly described.

The Shake Method with Hide Powder.—One of the drawbacks to the bell filter is undoubtedly the varying composition of the filtering liquid at different heights in the bell, and the attendant absorption of non-tannins, and swelling due to acids. These difficulties may, to a

certain extent, be overcome by the shake process. The method is as follows (A.O.A.C., *Methods of Analysis*, 46, p. 80):—

Prepare 20 grms. of hide powder by washing in a No. 7 beaker with from 800 to 1000 c.c. of water, stir well and let stand one hour, filter the magma through linen, squeeze thoroughly by hand, and remove as much water as possible by means of a press, weigh the pressed hide, and take approximately one-fourth of it for moisture determination. Weigh this fourth carefully and dry to constant weight. Weigh the remaining three-fourths carefully and add them to 200 c.c. of the original solution; shake ten minutes, and squeeze the tanned hide through linen. Collect this filtrate, add 5 grms. of kaolin, free from soluble salts, stir well and filter through folded filter (S. and S. No. 590, 15 cm.), returning the first 25 c.c. Evaporate 100 c.c. of the clear filtrate. The weight of this residue must be corrected for the dilution caused by the water contained in the pressed hide powder. The shaking must be done in some form of mechanical shaker. The simple machine used by druggists, and known as the milk shake, is recommended. The method is chiefly of interest in that it introduces the shaking which has now become an integral part of the official process; but the results it gave were somewhat uncertain, and the difficulties caused by the introduction of water, and accompanying dilution of the liquid to be detannised, can be obviated by the use of a filter pump, or to a less extent by the use of the Palmer process, which is in reality a modification of the shake method just described.

The Palmer Modification of the Hide Powder Method.—This process is very useful in works for the rapid carrying out of comparative analyses, but the results obtained do not, of course, agree with those given by the official process. The detannisation of the solution is carried out as follows:—

Five grms. of hide powder are placed in a beaker, and from 30 to 50 c.c. of the tannin solution are added. The mixture is thoroughly stirred, and allowed to stand for about 10 minutes, after which it is filtered through linen or muslin and squeezed as dry as possible. It is then replaced in a beaker and mixed with 50 or 60 c.c. of the liquor, the mixture being poured into a wide burette, at the bottom of which is placed a plug of cotton-wool. The burette is now corked and thoroughly shaken for some minutes, after which it is allowed to stand for from 10 to 15 minutes to complete the detannisation. The liquid is then drawn off slowly through a tap, the cotton-wool acting as a filter, and the liquid part of the filtrate is evaporated for soluble non-tannins.

This process may be very conveniently combined with the Löwenthal method, the detannisation being simpler than that by gelatine, and approximating more closely to tan-yard conditions. ■

In this case the original liquor and a portion of the detannised filtrate are titrated with potassium permanganate and indigo carmine as already described.

Parker and Payne's Method.—This method was originally proposed as an attempt to overcome one of the chief difficulties in the use of hide powder, namely, that it absorbs gallic acid and similar substances, and co-estimates them with tannic acid. The authors use as a detannising agent an acid solution of collin, the latter being a product of the hydrolysis of gelatine by caustic alkali, or perhaps, as the authors imagine, gelatine in which the lime base is replaced by soda. Further, neither the tannins nor soluble non-tannins are weighed, but measured by titration with a solution of lime. The following details of the test are taken from the author's paper (*J.C.S.I.*, 1904, 648). The following solutions are required:—

(a) A fifth normal solution of lime.

(b) An acid solution of collin.

Preparation of Lime Solution.—Although lime is only slightly soluble in distilled water, it is more readily soluble in the presence of sugar. An aqueous solution of cane sugar is shaken with finely powdered lime and, after settling, is filtered and titrated with standard acid and phenolphthalein, and diluted till exactly fifth normal. It must be carefully protected from the action of atmospheric carbonic acid.

Collin Solution.—Sixty grms. of a good commercial gelatine are soaked in about 500 c.c. of distilled water and warmed until dissolved. One hundred and twenty c.c. of normal caustic soda solution are then added, and the mixture is warmed on the water-bath for 20 minutes at 90° C. The precipitated calcium and other salts are removed by filtration through linen, and the filtrate is placed in a 500 c.c. flask, cooled, and made up to the mark. One hundred c.c. of the cold solution are then titrated with normal hydrochloric acid and phenolphthalein, and from the result obtained the amount of acetic acid necessary to neutralise the remainder of the solution is calculated and added. One c.c. of chloroform is added as a preservative, and the whole made up to exactly 1 litre, thus giving approximately a 5 per cent. solution of neutral collin.

The tanning extract having been filtered, 200 c.c. are placed in a stoppered cylinder, and 300 c.c. of the calcium hydroxide solution are added; after which the cylinder is well shaken and allowed to stand for three hours, with occasional further shaking. Digallic acid is precipitated in the form of a basic insoluble compound, the reaction being almost complete in one hour, and quite within three hours. In the case of some sumach liquors, however, a greater quantity of lime is absorbed during the first four or five minutes than at the end of the three hours, this, possibly, being due to the fact that calcium gallate has been thrown out of solution together with the tannate, and that it gradually re-dissolves. At the end of the three hours the liquid is rapidly filtered, and 100 c.c. of the filtrate titrated with fifth normal acid and phenolphthalein to obtain the volume of unused lime solution. This multiplied by 5 and deducted from 300, the amount originally taken, gives the volume of

fifth normal lime solution absorbed by 200 c.c. of the original liquor. This figure is known as the total absorption, and is calculated into its equivalent of tannic acid, 1 grm. of which will exactly absorb 125 c.c. of fifth normal calcium hydroxide, corresponding with the equation—



Thus one molecule of anhydrous digallic acid forms an insoluble basic salt with four molecules of calcium hydrate, but this only takes place if the lime water is present in considerable excess. If a large excess is not present, other salts of varying composition are formed which prevent correct estimation. Barium hydroxide may be used, but not sodium or potassium hydrates, since the latter do not form insoluble precipitates. Having obtained the total absorption figure, a portion of the solution is detannised and filtered, and again titrated with lime solution, the difference between the total lime absorption and the lime absorption of the detannised filtrate giving the tannins which have been removed by the collin. Two hundred c.c. of the original liquor are placed in a stoppered cylinder, and 100 c.c. of collin solution and 100 c.c. of fifth normal acetic acid are added and the mixture is thoroughly shaken. The tannins are completely precipitated as amorphous leather, which may be filtered off, dried, and weighed, thus giving some idea of the leather-producing properties of the material. After an interval the mixture is filtered, and 200 c.c. of the filtrate are shaken in a stoppered cylinder with 200 c.c. of fifth normal lime solution, the shaking being continued at intervals during an hour.

The mixture is then filtered, and the lime absorption of the filtrate is found by titration. This gives, after deducting the amount of acetic acid added, the absorption *minus* the tannins which have been removed, and hence, by difference, the amount of true tannins can be calculated. Great care must be exercised in the measurement of the solutions, since 1 c.c. in the lime absorption figure makes a considerable difference in the final result. The following example shows the method of obtaining the tannin figures:—

Ten grms. of a sumach were extracted in the ordinary way and made up to 1 litre, and filtered as usual.

TABLE XXXVI.

Total Absorption.

Precipitate the tanning matters in the manner described above.

100 c.c. of filtrate	= 45 c.c. $\frac{N}{5}$ acid.
∴ 500 c.c. = total quantity = 200 c.c. original extract	= 225 c.c. $\frac{N}{5}$ acid.
∴ Lime absorbed	= 300 - 225 c.c. = 75 c.c.
∴ Lime absorbed (litre extract)	= 375 c.c. $\frac{N}{5}$ Ca(OH) ₂ .

$$\begin{aligned} \therefore 10 \text{ grms. sumach} &= 375 \text{ c.c. } \frac{N}{5} \text{ Ca(OH)}_2 \\ &= \frac{375}{125} = 3 \text{ grms. tannin.} \end{aligned}$$

\therefore 100 grms. sumach contain 30 grms. tannin matters, including colouring and other organic matters, which are estimated by the "Acid Absorption."

Acid Absorption.

200 c.c. extract	}	are mixed together as described, and filtered.
100 c.c. $\frac{N}{5}$ acetic acid and		
100 c.c. collin solution		
400 c.c. total volume.		
200 c.c. of above filtrate contain	100 c.c. extract.	
To this is added	200 c.c. $\frac{N}{5}$ Ca(OH) ₂ .	
After filtering 100 c.c.	- 40.5 c.c. $\frac{N}{5}$ HCL.	
\therefore Whole volume = 400 c.c.	= 186 c.c. $\frac{N}{5}$ HCL.	
<i>i.e.</i> Lime absorbed by 100 c.c. of original extract	= 200 - 186, <i>i.e.</i> 14 c.c.	
\therefore 1000 c.c. extract	= 140 c.c. $\frac{N}{5}$ Ca(OH) ₂	
	= $\frac{140}{125}$ grms. tannins	
	= 1.12 grms. non-tannins, mainly colouring matters and certain organic acids	

Thus the true tannin matters are given by the difference of these two figures, and equal 30.0 - 11.2, *i.e.* 19.8 per cent.

In the hide-powder process the volatile acids are largely driven off by drying the residues in the air-bath, and are only partly estimated in the analysis; but by the method above described they can be accurately determined. For this purpose the total absorption value of a liquor is taken out, and a further sample slowly evaporated to dryness on the water-bath, re-dissolved in water, and a second absorption taken out; the difference gives the amount of volatile acids contained in the sample.

The usefulness of the method may be further applied in the detection of admixtures in tanning materials. "These may in part be obtained from the ratio of the true tannins to the acid, from which fairly accurate quantitative results are easy to calculate. But the qualitative detection of admixtures is extremely easy, owing to the colour reaction given, on the one hand, when the tannin solution is added to the lime solution, but still more marked when the detannised solution is added to the lime water, the colours for each of the commercial tanning materials being very characteristic, ranging from mangrove, which is a deep red, mimosa, which is a lavender colour, to chestnut, which has a mahogany shade, and myrobalans, which gives a brown yellow, rapidly changing to a brilliant green; but if the

sumach be adulterated with any quantity of either pistacia or tamarix, the colour produced is a deep brown, with no trace of green colour on standing."

Colour Weight.—Messrs Parker and Payne also claim to be able to determine the "colour weight" of materials by determining the weight and composition of the collin precipitate. They assume that 12 parts of tannin combine with 13 of collin, and from the amount of the true tannin figure given by the analysis calculate the weight of collin precipitate this would produce. This is generally less than that actually found by weight, the difference being due to colour weight.

Parker and Payne's process has been strongly criticised by Procter, who concludes that it is unreliable as a method of analysing tanning materials, although it may be useful for controlling operations in the tanyards. Trotman and Wood have also shown that the collin solution, as prepared by Parker and Payne, is a complex mixture of gelatones and peptones of varying composition and properties.

Precipitation with Organic Bases.—Among methods which attempt to do away with the use of hide powder, that depending on the insolubility of strychnine tannate has already been mentioned (p. 106). It appears to be one of the few proposed which really differentiate between gallic and tannic acid. In the adaptation of this method to tanning materials, the following process was used, the results of which compared very well with those given by hide powder in the case of those materials containing chiefly gallotannic acid. Where much gallic acid was present the result was naturally much lower, though probably more correct. The tanning materials were extracted in the special apparatus already described (p. 114), and the alcoholic extract treated as follows:—

The solvent is evaporated to about 50 c.c., then poured into a 100 c.c. flask, and made up to the mark with water. This will cause the precipitation of resins and similar bodies which have been extracted by the alcohol. These are filtered off, and the tannic acid is estimated in 25 c.c. of the filtrate. A further 25 or 50 c.c. is evaporated to dryness, and the residue weighed to determine the total soluble matter. The tannic acid in the filtrate is estimated as follows:—25 c.c. of the extract are placed in a 250 c.c. flask and diluted with water. 0.25 grm. of strychnine is then weighed out and dissolved in about 50 c.c. of alcohol. To this an equal volume of water is added, the mixture cooled and added to the tannic acid, the contents of the flask being diluted to the mark, and thoroughly mixed. If the precipitation be not carried out in the above manner, it is found that the strychnine tannate will not come down in a sufficiently flocculent form, and will be difficult to filter.

The contents of the flask are now filtered through a weighed Gooch crucible. The crucible used has a diameter of from 1 to 2 in. at the bottom, and may be made of platinum or porcelain. Having fixed it to the filter pump, a thin mat of asbestos pulp is prepared in the usual way,

dried over the blowpipe flame and weighed. The tannates, after filtration, are partly dried by means of a current of air, the deliquescence being completed in a vacuum oven, by which decomposition is avoided, this occasionally taking place if dried in an air or water oven. The dry precipitate contains 49.05 per cent. of tannic acid.

Parker and Payne have suggested precipitation with excess of an alkaloidal salt and titrating the liberated acid after filtering off the precipitate. A. W. Hoppenstedt (*J. Amer. Leather Chem. Assoc.*, 1907, pt. 6, pp. 175-179) suggests a method depending on the optical activity of certain bodies, notably cinchonine sulphate, which precipitates tannic acid. The optical rotation for pure tannic acid having been found by experiment, the factor is applied to the analysis of tannin solution in the following way:—Fifty c.c. of a cinchonine sulphate solution are mixed with an equal volume of a pure tannic solution, and after filtering off the precipitated tannins the optical rotation of the filtrate is measured. At the same time 50 c.c. of the alkaloidal solution are diluted with 50 c.c. of distilled water and the optical rotation again measured. From these readings the factor for tannic acid is calculated, which can then be applied to the analysis of tanning materials. Except in the case of bodies containing "reds" the results agree closely with those of the optical method.

Absorption by Metallic Compounds.—S. C. Dodge (*J. Amer. Leather Chem. Assoc.*, 1907, pt. 2, pp. 38-39) uses lead carbonate to precipitate the tannins. After shaking the liquor with this compound he filters and determines the non-tannins in the filtrate in the usual way.

H. Wislicenus (*Z. anal. Chem.*, 1905, 96-106) advocates the use of "spongy" alumina for the detannisation of tanning materials. It is prepared by the oxidation of aluminium powder by dilute caustic soda solution in the presence of a trace of mercury. The resulting hydroxide is washed with ether and ignited. In a more recent paper (*Collegium*, 1907, 157-163, 169-175) the author claims advantages for "spongy" or "sprouted" alumina over hide powder, since its quality is less variable, and it is not affected by the temperature or humidity of the atmosphere. It contains no soluble matter; far less is required for each determination; and, after each experiment, the alumina can be recovered by heating to dull red heat.

In the analysis of a tanning material the moisture is determined on about 2 grms. In making up the solution of tanning material for analysis, such a quantity is taken as will give 0.3 per cent. of the tannin. For filtration, four or five filter papers ("S. and S. 602 extra hard") are wrapped round a perforated glass tube similar in shape to a filter candle. These are fastened by an elastic band, and the liquor is sucked through by a water pump. After the filtration the papers are thrown away, and fresh ones used for the next determination. One hundred c.c. of the original liquor for "total solids" and 100 c.c. of the filtered liquor for "total solubles"

are evaporated, and by deducting the latter from the former, the amount of "insolubles" is obtained.

For the estimation of "non-tannins" 2.5 grms. of "sprouted alumina" are placed in a cylindrical glass tube, the remaining space packed tightly by cotton wool. The tube is fitted with india-rubber bungs and glass tubes at either end, and is held in a perpendicular position by a clamp. The lower end is connected to a reservoir, which can be raised or lowered by a

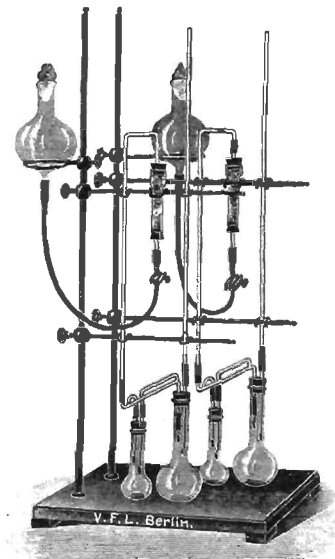


FIG. 28.

clamp, while the upper end is connected by a syphon tube to a flask standing on the bench. The liquor is introduced into the reservoir, which is then raised above the height of the alumina tube. The process is now simply one of syphoning, and should take from 5 to 6 hours, and when possible it is advisable to leave it over-night. The cotton wool being packed tightly in the tube prevents the process going on too rapidly. When about 110 c.c.s. have syphoned over, the apparatus is disconnected and 100 c.c.s. of the detannised liquor are evaporated to dryness. The result

gives the non-tannins, and this figure when deducted from the "total solubles" gives the "tannin substance." The apparatus used is shown in fig. 28.

Determination by Oxygen Absorption.—Another interesting process (W. Vaubel and O. Scheuer, *Z. angew. Chem.*, xix. 2130-2133, 1906, and *J.S.C.I.*, 1907, 59) depends on the power which tannic acid has of absorbing oxygen. The absorption depends directly upon the concentration of the sodium hydroxide solution used, and the authors measured it under constant conditions, both by volumetric and gravimetric methods. For the former a jointless wash-bottle is used, both tubes being provided with stop-cocks, and the shorter carrying a small separating funnel. The volume of the flask when filled to the two taps is known. A measured volume of a solution of pure tannic acid is then introduced into the flask, which has previously been filled with oxygen, and 100 c.c. of sodium hydroxide solution are added, the reagents and apparatus being kept at a constant temperature. The apparatus is now frequently shaken, and measured quantities of sodium hydroxide solution run in through the funnel, as required, to replace the absorbed oxygen, the volume of which is finally corrected for temperature and pressure. For the gravimetric method, which is preferable, sodium hydroxide solution is placed in a flask, to the neck of which is attached, by means of a glass stopper, a drying apparatus containing sulphuric acid, whilst through the side passes a tube through which oxygen can be introduced. The weight of the flask, alkali, and acid having been ascertained, the stopper is removed, and 0.5 gm. of pure tannic acid is added. The flask is then closed, and oxygen passed through until no further increase in weight is observed. The experiment is carried out at a constant temperature (12° to 18° C.), and in the absence of direct sunlight. The average oxygen values of tannic acid given by the volumetric and gravimetric methods are 0.3280 and 0.3092 respectively for 1 gm. of dry gallotannic acid. The volumetric method has been employed in the analysis of certain tanning materials, and the results obtained show fair agreement with those from hide powder, but further experiments are still necessary to finally establish the details of the process and the factors for the different tanning materials.

The Use of Formalin Gelatine.—Schmitz-Damout (*Analyst*, 1897, p. 248) has described a method in which hide powder is replaced by formalin gelatine with considerable success. He prepares the gelatine by saturating thick filter paper with a 10 per cent. solution and laying it upon glass rods to dry. It is then immersed for 24 hours in a 2 per cent. solution of formalin, after which the excess of liquid is pressed out and the saturated paper dried at 100° C. It is then ground into a powder and treated again with 2 per cent. formalin as before and re-dried. In order to free it from trioxymethylin it is digested with hot water until the washing gives no re-action for formalin with alkaline resorcin solution.

There is practically no soluble matter, and experiments made side by side with hide powder gave very satisfactory results.

Formalin Hide Powder.—Procter and Blockley (*J.S.C.I.*, 1903, p. 484) have experimented with hide powder treated with formalin and found that a satisfactory powder could be obtained by simply treating hide powder with an aqueous solution of formalin for 3 hours and subsequently washing it thoroughly and drying in a current of warm air.

The Chromed Hide Powder Method.—The observation that chromium compounds have the power of rendering gelatine insoluble and changing it to leather without destroying its capacity for absorbing tannins was soon suggested as the basis of an analytical method to replace the ordinary hide powder. An immense amount of work has been devoted to this subject, the final outcome of which is that the use of chromed hide powder is now firmly established.

The American Official Process.—The American leather chemists have for some time used a similar process which combines the use of chromed powder with the "shake method." The details of this process are as follows (*Collegium*, 1902, 72; *J.S.C.I.*, 1903, p. 130):—

I. **PREPARATION OF SAMPLE.**—Barks, woods, leaves, dry extracts, and similar tanning materials should be ground to such a degree of fineness that they can be thoroughly extracted. Fluid extracts must be heated to 50° C., well shaken, and allowed to cool to room-temperature.

II. **QUANTITY OF MATERIAL.**—In the case of bark and similar material, use such quantity as will give about 0.35 to 0.45 gm. tannins per 100 c.c. of solution, extract in Soxhlet or similar apparatus at 100° C. for non-starchy materials. For canaigre and substances containing like amounts of starch use temperature of 50° to 55° C., until near complete extraction, finishing the operation at steam heat. In case of extract, weigh such quantity as will give 0.35 to 0.45 gm. tannins per 100 c.c. of solution, dissolve in 900 c.c. of water at 80° C., let stand 12 hours, and make up to 1000 c.c.

III. **MOISTURE.**—Evaporations shall take place under precisely the same conditions as to contact with steam or a metallic plate, all dryings necessary after evaporation being done by one of the following methods, under precisely the same conditions, so that the different residues of each analysis may occupy the same shelves in the drying oven:—

1. For 8 hours at 100° C. in the steam oven.
2. For 6 hours at 100° C. in an air-bath.
3. For 5 hours at 100° C. *in vacuo*.

IV. **TOTAL SOLIDS.**—Shake the solution, and, without filtering, immediately measure out 100 c.c. with a pipette, evaporate in a weighed dish, and dry to constant weight, at the temperature of boiling water. Dishes should be flat-bottomed, and not less than 6 cm. in diameter.

V. **SOLUBLE SOLIDS.**—Single-pleated filter paper (S. and S. No. 590, 15 cm.) shall be used. To 2 grms. of kaolin add 75 c.c. of the tanning

solution, stir, let stand 15 minutes, and decant as much as possible. Add 75 c.c. more of the solution, pour on filter, keep filter full, reject the first 150 c.c. of filtrate, evaporate the next 100 c.c. and dry. Evaporation during filtration must be guarded against.

VI. NON-TANNINS.—Prepare 20 grms. of hide powder by digesting 24 hours with 500 c.c. of water, and adding 0.6 gm. chrome alum in solution, this solution to be added as follows: one-half at the beginning and the other half at least 6 hours before the end of the digestion. Wash by squeezing through linen, continue the washing until the wash-water does not give a precipitate with barium chloride. Squeeze thoroughly by hand, and remove as much water as possible by means of a press, weigh the pressed hide, and take approximately one-fourth of it for moisture determination. Weigh this fourth carefully and dry to constant weight. Weigh the remaining three-fourths carefully and add them to 200 c.c. of the original solution; shake 10 minutes, throw on funnel with cotton plug in stem, return until clear, then add 2 grms. of kaolin and filter through 590 paper till clear and evaporate 100 c.c. and dry. The weight of this residue must be corrected for the dilution caused by the water contained in the pressed hide powder. The shaking must be done in some form of mechanical shaker. The simple machine used by druggists, and known as the milk-shake, is recommended.

Provisional Method.—To 14 grms. of dry chromed hide powder in a shaker glass add 200 c.c. of the tannin solution, let stand 2 hours, stirring frequently, shake 15 minutes, throw on funnel with a cotton plug in the stem, let drain, tamp down the hide powder in the funnel, return the filtrate until clear and evaporate 100 c.c.

VII. TANNINS.—The amount of these is shown by the difference between the soluble solids and the corrected non-tannins.

VIII. TESTING HIDE POWDER.¹—(a) Shake 10 grms. of hide powder with 250 c.c. of water for 5 minutes, strain through linen, squeeze the magma thoroughly by hand; repeat this operation three times, pass the last filtrate through paper (S. and S. No. 590, 15 cm.) till clear, evaporate 100 c.c. and dry. If this residue amounts to more than 10 mg. the hide must be rejected.

(b) Prepare a solution of pure gallotannin by dissolving 6 grms. in 1000 c.c. of water. Determine the total solids by evaporating 100 c.c. of this solution and drying to constant weight. Treat 200 c.c. of the solution with hide powder exactly as described in paragraph vi. The hide powder must absorb at least 95 per cent. of the total solids present. The gallotannin used must be completely soluble in water, alcohol, acetone, and acetic ether, and should not contain more than 1 per cent. of substances not removed by digesting with excess of yellow mercuric oxide on steam-bath for two hours.

¹ This paragraph is now omitted from the official process (*J.S.C.I.*, 1903, p. 130).

IX. TESTING NON-TANNIN FILTRATE.—(a) *For Tannin*.—Test a small portion of the clear non-tannin filtrate with a few drops of a 1 per cent. solution of Nelson's gelatine. A cloudiness indicates the presence of tannin, in which case repeat the process described under VI., using 35 instead of 20 grms. of hide powder.

(b) *For Soluble Hide*.—To a small portion of the clear non-tannin filtrate add a few drops of the filtered tannin solution. A cloudiness indicates the presence of soluble hide, in which case repeat the process described under VI., giving the hide powder a more thorough washing.

The temperature of solutions shall be between 16° and 20° when measured or filtered. All dryings should be made in flat-bottomed dishes of at least 6 cm. diameter. S. and S., No. 590 15 cm. filter paper should be used in all filtrations.

According to Procter and Bennett (*Collegium*, 1907, 15), the principal objections to the American method are the long time required for chroming the hide powder, which must be freshly done for each set of analyses, and the tedious method of determining the water correction. Further, the percentage of chrome absorbed by the powder does not appear sufficient to secure insolubility of the powder under unfavourable conditions, while the large amount of unabsorbed chrome salt leaves scope for great variations in the amount of acid taken up. The latter point has been shown to largely affect the absorptive powers of the powder. The maximum amount of chromic oxide the American powder can contain is 0.45 per cent. The authors regard 0.75 to 1 per cent. as being required to prevent variations due to the quality of the unchromed powder.

J. R. Mardick (*Collegium*, 1905, 113), as the result of an investigation, raises the following objections to the American official process:—

1. The shaking creates abnormal conditions in which the hide powder in some cases goes into solution and creates a favourable medium for the absorption of non-tannins.
2. The quantity of material used for analysis (*i.e.*, 3 grms. tannin per litre) is too small, and the hide powder too much. The result is that more gallic acid and non-tannins are absorbed by the powder. The solution should contain 10 grms. per litre.
3. There must be an appreciable error in making the analysis at the room-temperature. 20° C. would correspond more to actual practice.
4. In the chroming of the hide powder, 3 grms. of chrome alum per 100 grms. of powder is not enough to make the hide matter insoluble. It is better to use basic chromium sulphate or chloride in quantities containing 1 per cent. of chromic oxide per 100 grms. of powder.

The same author (*loc. cit.*, p. 115) makes the following suggestions for a modified method of analysis:—

¹ This paragraph is now omitted from the official process (*J.S.C.I.*, 1903, p. 130).

Preparation of Hide Powder.—Digest 100 grms. of hide powder in 1000 c.c. of water for 2 hours; add 8 grms. of chrome alum, changing previously to basic chromium sulphate by boiling 50 c.c. of water to 25 c.c. with 1 gm. of soda crystals. After 12 hours, squeeze through linen, and wash five times with distilled water. In the last washing add 10 c.c. formaldehyde (30 per cent.), and let it stand 2 hours before squeezing. By a press, get as much water out of it as possible, and use 25 grms. of this hide powder for analysis, and from 1 to 2 grms. for moisture determination.

Quantity of Material.—For the purpose of analysis the following quantities are recommended:—

TABLE XXXVII.

	Grms.		Grms.
Hemlock Bark,	50	Sumach,	25
Oak Bark,	50	Spent Tan,	100
Oak Wood,	100	Amazona Bark,	25
Quebracho Wood,	35	Chestnut Wood,	100

EXTRACTS.

	Grms.
Chestnut Wood,	40
Quebracho (solid),	15
Quebracho (liquid),	30
Gambier,	20
Hemlock,	35

After extracting the tannin materials from the above, the solution must be made up to 1000 c.c. and measured at 20° C.

Total Solids.—Shake the solution thoroughly, and measure at 20° C., and dry (at from 102° C. to 103° C.) for 3 hours.

Soluble Solids.—To 1 gm. washed kaolin add 5 c.c. of tannin solution; stir until thoroughly mixed; then add 70 c.c. of the same solution, stir and pour on filter (S. and S. No. 590, 15 cm.). Keep the filter full, reject the first 100 c.c. of the filtrate, and evaporate the next 50 c.c. on water-bath, and dry from 102° C. to 103° C. for 3 hours.

Non-Tannins.—To 25 grms. of hide powder in a shake-glass add 100 c.c. of tannin solution, stir, and crush with a spatula the large particles on the side of the glass; after it has stood 10 minutes, stir $\frac{1}{2}$ minute; after 15 minutes' standing, stir again, and throw on a double-folded cheese-cloth; squeeze out as much liquid as possible; filter in same way as in soluble solids; evaporate 50 c.c. on water-bath; then dry at 102° C. to 103° C. for 3 hours.

Precautions.—In all quantitative work of tannin analysis, (a) evaporation during filtration must be guarded against both in the funnel and in the receiver of the filtrate. (b) After evaporating the solutions on water-bath, the dishes which contained the tannin must be dried at 102° C. to 103° C. for 3 hours, and must be weighed only once. (c) In the

analysis of gambier, sumach, myrobalans, quebracho, and other sour liquors, it will be necessary to let the tannin solution stand with the hide powder for a longer time (about 60 minutes instead of 30), with occasional stirrings.

He states that, in order to get concordant results corresponding to those of tannery practice, the following conditions should be observed:—

- (a) The solution ought to contain 10 grms. of tannins per litre.
- (b) The analysis ought to be carried out at about 20° C.
- (c) There ought to be just enough hide powder to absorb all the tannins and no more; 25 grms. of hide powder for 100 c.c. of liquor would answer for this purpose.
- (d) The maceration method is far preferable to the shake method, for known mechanical reasons, as the friction created by shaking increases the tendency of hide powder to go into solution.
- (e) In order to make it nearly insoluble, the hide powder ought to be chromed with 8 grms. of basic sulphate of chromium for 100 grms. of dry powder.

Some of these criticisms are no doubt reflected in a resolution passed at the third annual meeting of the American Leather Chemists' Association (*J.S.C.I.*, 1907, 330), viz., that the present method of total soluble determination in tanning materials be replaced by the following:—

“To 1 gm. of kaolin in a beaker add 75 c.c. of tannin solution, stir and pour on 590 S. and S. 15 cm. pleated paper. Return filtrate to the paper for 1 hour, keeping the filter full. At the end of the hour pour the solution from the filter. Bring 800 c.c. of it to a temperature of 20° C., refill the filter with this solution, and begin to collect the filtrate for evaporation as soon as it becomes clear, keeping the filter full.”

Other resolutions dealing with points raised in Mardick's paper were referred to a committee for consideration.

The use of chromed hide powder by no means does away with the necessity for standard conditions, particularly with reference to the chroming of the powder. Paessler and Appellius and others have shown that the extent to which it is chromed, and other factors, such as acidity, materially affect its power of absorbing both tannins and non-tannins. Nihoul and others have shown that lightly chromed powders are much more satisfactory than heavily chromed, provided sufficient chromic oxide be present to prevent rapid putrefaction. Many chemists originally objected to the use of chromed powder, chiefly on this account. It will not keep if lightly chromed, and if heavily chromed is unsatisfactory in use. The fact that certain non-tannins are absorbed alike by chromed powder and ordinary hide powder has been pointed out by Procter and Elockley (*J.S.C.I.*, 1904, 482), who, however, conceded the contention of the supporters of the use of chromed powder that it gave rise to fewer errors than other methods, but concluded that the difficulty attending its preparation

for each separate analysis made it troublesome for occasional work, and that the amount of water left in it largely affected the results. The chromed powder used was prepared by the American process, at the rate of 3 grms. of chrome alum per 100 grms. of powder. The following tables give the results obtained by Procter and Blockley. The first column gives the matter weighed out for each experiment, the second the weight of residue given by 100 c.c., from which the dry or non-volatile matter can be calculated. The remaining seven columns give the total soluble, the non-tannins, and tannins in percentages of the dry total soluble matter of the "tannin" employed; and the effect of the added non-tannins is obtained separately by deducting the corresponding figure given by the determination of the tannins alone. In columns 10, 11, and 12 is given the proportion of added non-tannin substance estimated as tannin, calculated on the actual dry non-tannin matter in excess of the 100 per cent. reckoned for the "total soluble" of the "pure" tannin.

TABLE XXXVIII.

Effect of Addition of Various Non-tannins to Gallotannic Acid.

Material employed.	Grms. per Litre.	Grms. Dry Soluble per 100 c.c.	Percentage on Dry Gallotannic Acid Taken.						Percentages of Dry Non-Tanning Substance estimated as Tannin.				
			Total Soluble.	Filter Method.		Chromed Powder.		Washed Powder.		Filter Method.	Chromed Powder.	Washed Powder.	
				Tannins.	Non-Tannins.	Tannins.	Non-Tannins.	Tannins.	Non-Tannins.				
1. Gallotannic acid,	4.6	0.408	100.0	95.1	4.9	90.1	9.9	57.4	12.6	
2. Gallotannic acid,	4.6	0.808	198.0	180.6	18.0	130.6	58.4	130.6	67.4	86.6	50.6	44.0	
Gallic acid,	4.4			104.6	94.4	80.9	112.1	85.6	113.4	9.6	-3.2	-1.8	
3. Gallotannic acid,	4.6	0.812	199.0	153.6	95.5	58.1	90.3	63.3	58.5	65.1	0.7	0.4	2.0
Dextrin,	4.5												
4. Gallotannic acid,	4.6	0.420	102.8	92.0	10.8
Glucose,	2.5												
5. Gallotannic acid,	4.6	0.500	122.5	117.3	5.2	104.4	18.1	101.9	20.6	98.7	63.6	64.4	..
Glac. acetic acid,	3.0												
6. Gallotannic acid,	4.6	0.526	128.9	120.5	8.4	113.7	15.2	112.7	16.2	87.9	81.7	87.5	..
Quinol,	2.5												
7. Gallotannic acid,	4.6	0.438	100.0	95.3	4.7	86.3	13.7	85.8	14.2
8. Gallotannic acid,	5.0												
Catechol,	2.5	0.574	131.7	140.8	8.0	132.0	16.8	128.8	29.0	93.2	93.7	88.1	
9. Gallotannic acid,	5.0	0.657	150.1	142.2	7.9	110.3	39.8	111.2	38.9	93.6	48.1	48.9	..
Gallic acid,	2.5												
10. Gallotannic acid,	5.0	0.540	123.4	116.5	6.9	96.9	26.5	99.0	24.4	90.6	45.7	50.4	..
Gallic acid,	1.25												
11. Gallotannic acid,	5.0	0.660	150.7	145.6	5.1	124.2	26.5	118.6	32.1	99.2	75.0	64.7	..
Catechin,	2.5												

The controversy about the use of chromed hide powder has centered chiefly round the following points, namely, whether the highly or lightly chromed powder should be used, and whether a filter bell or maceration or shake method of detanning should be employed. It is impossible within the limits of available space to describe all the proposals that have been made and some of which have chiefly a historic interest; but some other

typical methods will be described, and finally the official method as recommended by the committee of the I.A.L.T.C., which has recently issued its report.

TABLE XXXIX.

Effect of the Addition of Various Non-tannins to Quebracho.

Material employed.	Grms. per Litre	Grms. Dry Soluble per 100 c.c.	Percentage on Dry Quebracho Tannin taken						Percentages of Dry Non-Tanning Substance estimated as Tannin.			
			Total soluble.	Filter Method.		Chromed Powder.		Washed Powder.		Filter Method	Chromed Powder.	Washed Powder.
				Tannins.	Non-Tannins	Tannins	Non-Tannins	Tannins.	Non-Tannins			
1. Quebracho tannin.	5.0	0.442	100.0	96.1	3.9	93.9	6.1	92.0	8.0
2. Quebracho tannin.	5.0	0.837	189.4	173.1	16.3	136.2	51.2	135.2	54.2	89.4	49.6	48.3
Gallic acid.	4.4											
3. Quebracho tannin.	5.0	0.843	190.8	101.0	89.8	88.3	102.5	88.3	102.5	5.4	-6.2	-4.1
Dextrin.	4.5											
4. Quebracho tannin.	5.0	0.651	147.2	94.2	53.0	90.6	56.6	90.1	57.1	-4.0	-7.0	-4.0
Glucose.	2.5											
5. Quebracho tannin.	5.0	0.470	100.3	97.5	8.8	57.0	..
Gluc. acetic acid	5.0											
6. Quebracho tannin.	5.0	0.356	125.0	121.3	4.6	112.2	13.1	115.0	10.9	97.3	73.0	88.8
Quinol.	2.5											
7. Quebracho tannin.	5.0	0.584	132.2	125.1	7.1	123.2	14.0	120.3	12.2	90.1	100.5	87.0
Catechol.	2.5											
8. Quebracho tannin.	5.0	0.440	100.0	94.9	5.1	88.6	11.4	89.1	10.9
Catechol.	2.5											
9. Quebracho tannin.	5.0	0.536	126.4	117.8	8.6	110.9	15.5	108.2	18.2	86.7	84.5	72.3
Catechol.	2.5											
10. Quebracho tannin.	5.0	0.668	151.8	144.3	7.5	115.2	36.6	118.4	33.4	95.4	51.4	56.6
Gallic acid	2.5											
11. Quebracho tannin.	5.0	0.540	122.7	115.3	7.4	98.8	23.9	100.7	22.0	89.9	44.9	51.1
Gallic acid.	1.25											
12. Quebracho tannin.	5.0	0.646	146.8	139.8	7.0	117.0	29.8	123.4	24.4	95.9	60.7	71.2
Catechin.	2.5											

Paessler's Method—Paessler's method is typical of those employing lightly chromed hide powder, and, in addition, he uses it dry and in connection with the filter bell. The chromed powder merely reduces the swelling in the bell, and the tannin absorption is more complete and hence the non-tannin figures more correct; further, according to Paessler and Appellus (*J.S.C.I.*, 1907, 213), lightly chromed hide powder gives better results in the filter bell than either ordinary powder or heavily chromed dry powder, while it also absorbs neither grape sugar, cane sugar, nor dextrin, and much less gallic acid than heavily chromed powder. The authors gave the following methods for the manufacture of lightly chromed powder to be used in the filter bell:—

1. Five hundred grms. of unacidified hide powder are churned with 10 litres of water, and 15 grms. of chrome alum dissolved in 500 c.c. of water are added at intervals, the chroming extending over 3-4 days. The mass is squeezed, and well washed with distilled water until free from sulphate, when it is dried and ground.

2. To one kilo. of hide, use 10 grms. of chrome alum and $2\frac{1}{2}$ -3 litres of water, the chrome alum solution being added at intervals. After chroming, the hide is twice drummed with sodium silicate solution (10

grms. of sodium silicate and 2.5 litres of water per kilo. of hide) to neutralise acidity, drummed again with fresh water, and then stretched in a frame to dry. After drying, the hide is ground.

Weiss (*Der Gerber*, xxxi. 260-261, 275-278, 1905; *J.S.C.I.*, 1905, 1129) proposed a maceration method which has been for some time in use at the Vienna Research Institution. The powder is prepared by digesting 1000 grms. of cellulose-free ordinary hide powder with a solution of basic chromic sulphate made by neutralising 150 grms. of chromic alum with 24 grms. of sodium carbonate. After chroming, the powder is washed with water till free from sulphuric acid, and then the excess of water is squeezed out and the residual powder dried and ground. For detanning, 8 to 10 grms. of the dry powder are moistened with 30 c.c. of water and allowed to stand for 1 hour. One hundred and twenty c.c. of tannin solution are then added, the mixture being thoroughly shaken and allowed to stand over-night in a stoppered cylinder or bottle. Next morning the mixture is filtered and 100 c.c. evaporated for the determination of non-tannins, a correction for the quantity of water added being made by multiplying the weight of residue by $\frac{5}{4}$. With the exception of some highly coloured tannin liquors, such as mangrove, 10 grms. of powder will usually be sufficient; if not, the solutions are diluted with an equal volume of water before use.

Wood and Holmes (*Collegium*, 1906, 301), and **Kopeccky** (*Collegium*, 1905, 100), recommend the use of ordinary chromed box-calf shavings containing 5.7 per cent. of chromic oxide. These are neutralised and washed with distilled water till free from soluble matter, after which they are squeezed as free as possible from water and used in the wet state, since, if once dried, it is impossible to wet them down again. For the detanning of tanning liquors a quantity of the shavings containing 5 grms. of dry chromed skin is stirred for an hour by a small motor with 500 c.c. of the tannin solution and the mixture allowed to stand for about 15 hours. The precipitated leather is then strained off through muslin and the solution filtered and a portion of it evaporated for determination of soluble matter, a correction being made for the amount of water added with the chromed shavings. The latter generally contain about 78 per cent., but the exact percentage must be determined by analysis.¹

Kopeccky's Method.—**Kopeccky** (*Collegium*, 1906, 211-214, 217-229) uses a heavily chromed powder which he prepares by chroming pieces of calf-pelt and drying these and grinding them to powder in a mill. His formula is as follows:—

Sixteen lbs. of limed hide-bellies are delimed by means of a sour bran drench, then properly washed and tanned with basic chrome liquor,

¹ These shavings are well adapted for control analyses in works, but they do not keep and cannot be wetted down when once dry. If kept for any length of time in the moist state they give abnormally high soluble non-tannins.

containing, calculated on wet pelt weight (*Blössengewicht*), 10 per cent. chrome alum ($K_2SO_4.Cr_2(SO_4)_2.24Aq.$), dissolved cold, and 3.5 per cent. washing soda ($Na_2CO_3.10Aq.$), dissolved separately and gradually added. This stock liquor was added gradually in small quantities to the pelt, placed in water in a revolving drum, and the tannage was completed in 18 hours. The chromed bellies, after lying for 12 hours, were neutralised with 3 per cent. borax for 1 hour, then washed three times in three changes of water, set out thoroughly, and slowly dried; and, before becoming completely dry, they were lightly staked. When dry they were ground in a toothed disc mill ("Favourita" mill, Glaeser & Co., Vienna) to a fine powder, which is called in this article "chromed hide powder." This powder after further washing, drying, and grinding is described as "washed chromed hide powder."

In detannising he wets down the hide powder with hot water, squeezing out excess and leaving about 70 per cent. of the residue. Thirty grms. of the wet powder are used for each detannisation, these being carried out in a wide-mouthed stoppered bottle by a maceration process. He gives the following methods of procedure:—

(a) Thirty grms. of the wet powder are weighed out and about three-quarters of this are added, with mixing, to 150 c.c. of the tannin solution, the mixture being allowed to stand with occasional vigorous stirring for 50 minutes. The remainder of the wet powder is then added and the mixture again macerated for 10 minutes.

(b) The whole 30 grms. are added at once to 150 c.c. of tannin solution and the mixture shaken for 10 minutes in a milk shake or similar machine. After maceration the mixture is filtered twice through a Dreverhoff No. 311 paper, after which 50 c.c. of the filtrate are evaporated to dryness and weighed, the result being corrected for the moisture present in the wet hide powder by multiplication by the factor—

$$\frac{150 + \text{water in 30 grms. powder}}{150}$$

For all practical purposes the water in 30 grms. of wet hide powder, if prepared by the above method, may be assumed to be 21 grms., which gives the factor of 1.14, variations between 69 and 71 per cent. of water being negligible. Some materials, such as quebracho and mangrove, require 40 instead of 30 grms. of wet powder, in which case the factor is 1.187. In a later paper (*Collegium*, 1906, Nos. 199 to 203) the same author gives a critical survey of the methods already proposed.

Using the filter bell he found that neutralised chromed powder absorbed more non-tannins than powder which is slightly acid. The same was true, up to a certain point, of heavily chromed powder, but a large amount of chromic oxide considerably reduces the absorptive properties of the leather.

In stirring and shaking methods, on the other hand, lightly chromed powder always showed slightly higher non-tannins than heavily chromed powder, perhaps due to dissolved hide-substance.

Kopecky found that neutralised chromed hide powder absorbed more gallic acid than acid chromed powder, and since the same is observed with heavily chromed powder, thinks the high absorption may be due to neutral Cr_2O_3 , unneutralised powder containing more or less hydrolysed chromic sulphate.

In the filter-bell method Kopecky believes that acids are given up by the portion of powder in which absorption of tannins takes place and then absorbed again by the unused powder in the upper part of the bell. In the macerating and shaking methods less gallic acid will be absorbed and higher non-tannin figures obtained. The fact that when in the latter method the powder is added in portions to the tannin solution lower non-tannins result seems to support the theory.

Kopecky concludes that the use of chromed hide powder in a filter bell is not advantageous, giving results no better than are obtained with the Freiberg powder and far from expressing the actual value of tanning materials. He does not favour acid chromed powder, much of the trouble experienced with Freiberg powder being due to its acidity. If acid must be used, acetic is the least objectionable, whether for acidifying powders or solutions. Lactic acid causes the residues to vary so in weight as to be valueless unless the amount of acid in the residue is actually estimated as suggested by Procter (*L.I.L.B.*, 126).

He finally suggests as a method to take the place of the bell-filter method one based upon the following results of his experiments:—

A. Preparation of chromed powder by chroming felt with basic chrome alum liquor, neutralising, washing, shredding, powdering and washing the powder free from soluble matter. Fresh batches of powder to be tested by a fixed method.

B. Soaking of chromed hide powder by pouring over it water at 60° and standing for an hour.

One of the following methods to secure uniform and rapid absorption of tannins in detannising:—

1. Soaking a known weight of squeezed powder in a measured volume of water containing a known quantity of formic or acetic acid for 1 hour.
2. To add 10 c.c. of dilute acetic acid solution (containing .75 gm. of acetic acid) to 150 c.c. of the tannin solution just before detannising.
3. To add 5 grms. of acetic acid per litre to all solutions (extracts and infusions) before making up to 1000 c.c.
4. To adopt the maceration method and add the whole quantity of wet powder at once to the tannin solution.
5. For residues of non-tannins (non-tannins, total solids and total solubles), evaporate 50 c.c. on the water-bath, and as soon as dry add 50 c.c. of distilled water and again evaporate to dryness.
6. To adopt a correction for the acidity of all extracts (even apparently unfermented, except mimosa D), reporting the same as acidity due

to non-volatile organic acids and calculating the same in terms of gallic acid, though not necessarily deducting this amount from the percentage of tanning matter found, unless both extract makers and tanners agree to it.

Parker and Bennett (*J.S.C.I.*, 1906, 1198), as a result of a critical examination of Paessler's and Kopecky's and the American method, conclude that the latter is superior to all others and strongly urge its adoption. With regard to the methods of Paessler and Kopecky they make the following criticisms:—

(1) *Kopecky's Powder and Method.*—The powder after a time loses its absorbency, not wetting back even after 24 hours' soaking. This can no doubt be accounted for by its being so heavily chromed, though possibly the neutralisation of the powder may act in this direction also.

The use of acidified solutions, which is necessary in the case of a neutral powder, is open to objection, especially in the case of treated extracts, the quantity of acid advocated by Kopecky (5 grms. per litre) being too large. Moreover, the addition of acetic acid to the solution of the extracts before making up to the mark introduces errors due to secondary reactions, such as the action of acid in tannin, this making an appreciable difference in the amounts of "total solids" and "total solubles" found, and further affects the quantity of "insolubles" and the tintometer readings. On the other hand, the addition of acid just before detanning involves another correction.

(2) *Paessler's Powder and Method.*—As the method consists in the use of the filter bell, it is open to all those strong objections which have been repeatedly urged against that method. Paessler's powder, though in some respects an improvement upon the unchromed, possesses a decidedly more marked affinity for "non-tannin" matter. Again, the keeping properties of this powder have not been tested thoroughly, and in view of the difficulties already observed in preparing dry chromed hide powders which will remain constant in quality, it is extremely important that this should be done before its adoption as an official powder.

The International Method of Tanning Analysis.—At a conference of the I.A.L.T.C., held in Frankfort in September 1906, a committee was appointed to inquire into the whole question of detanning of tanning liquors, and to recommend, if desirable, the adoption of a method to replace the present official one. The report of this committee was published in the *Collegium* (1907, 249), and is as follows, the method, therein described becoming official on 15th September 1907:—

General Regulations.—The Executive Committee have decided that any method which conforms to the condition of sections 1 to 4 of the following statement may be regarded as conforming to the recommendations of the International Commission on Tannin Analysis, but that members of the International Association must work according to the detailed directions contained in sections 5 to 8.

(1) The solution for analysis must contain between 3·5 to 4·5 grms. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C.

(2) *Total solubles* must be determined by the evaporation of a measured quantity of the solution, previously filtered, till optically clear both by reflected and transmitted light—that is, a bright object, such as an electric light filament, must be distinctly visible through at least 5 cm. thickness and a layer of 1 cm. deep in a beaker placed in a good light on black glass, or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss, when applied to a clear solution, a correction must be determined and applied, as described in section 6. Filtration must take place at a temperature between 15° C. and 20° C., or the actual temperature shall be stated in the Report.

(3) *Total solids* must be determined by drying a weighed portion of the material or a measured portion of its uniform turbid solution at a temperature not exceeding 100° C. *in vacuo* or 105° C. in air till constant. Moisture is the difference between 100 and the percentage of total solids; and insoluble, the difference between total solids and total solubles.

(4) *Non-tannins*—The solution must be detanned by shaking with chromed hide powder till no turbidity or opalescence can be produced in the clear solution by salted gelatine. The chromed powder must be added in one quantity equal to 6·0 to 6·5 grms. of dry hide per 100 c.c. of the tanning solution and must contain not less than 0·5 and not more than 2 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water not more than 5 mgr. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.

(5) *Preparation of Infusion*.—Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 grms. of tanning matter per litre and not less than 3·5 or more than 4·5 grms. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed and rapidly cooled to a temperature between 15° and 20° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials previously ground till they will pass through a sieve of five wires per centimetre are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50° C., and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than 3 hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected or reported separately, as "difficultly soluble" substances. The volume of liquid in the flask must after cooling be accurately made up to 1 litre.

(6) *Filtration*.—The infusion shall be filtered till optically clear (see sect. 2). No correction for absorption is needed for the Berkefeld candle or for S. & S. 590 paper, if a sufficient quantity (250-300 c.c.) is rejected, before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be determined in the following manner. About 500 c.c. of the same, or a similar, tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c.c. are evaporated to determine the "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate, and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c., and returning the remaining filtrate repeatedly; and, at the same time, to evaporate 50 c.c. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(*Note*.—It is obvious that an average correction must be obtained from at least five determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. & S. 605, 150 c.c. being rejected, to about 5 mgrms. per 50 c.c., and where 2 grms. of kaolin are employed in addition, to 7½ mgrms. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand for 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.

(It is proposed that the Commission should be asked to determine average corrections for the more important methods of filtration, and report at an early date.)

(7) *Detannisation*.—The hide powder employed shall be of a woolly

and not granular texture, thoroughly delimed, preferably with hydrochloric acid, and not requiring more than 5 c.c. of $\frac{N}{10}$ NaOH or KOH to produce a permanent pink with phenolphthalein on $6\frac{1}{2}$ grms. of the dry powder suspended in water; and the detanninisation shall be conducted in the following manner:—

The moisture in the air-dried powder is determined, and the quantity equal to 6.5 grms. actual dry hide powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken, according to the number of analyses to be made, and wetted back with approximately ten times its weight of distilled water. Two grms. per hundred of dry powder of crystallised chromic chloride¹ ($\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$) are now dissolved in water and made basic with 0.6 gm. Na_2CO_3 , by the gradual addition of 11.25 c.c. of $\frac{N}{1}$ solution, thus making the salt correspond to the formula $\text{Cr}_2\text{Cl}_3(\text{OH})_3$. This solution is added to the powder and the whole churned slowly for 1 hour. In laboratories where analyses are continually being made, it is more convenient to use a 10 per cent. stock solution, made by dissolving 100 grms. of $\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grms. of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water, and well mixing. Of this solution 20 c.c. per 100 grms. or 1.3 c.c. per 6.5 grms. of dry powder should be used. At the end of 1 hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed finally with distilled water, until on adding to 50 c.c. of the filtrate 1 drop of 10 per cent. K_2CrO_4 and 4 drops $\frac{N}{10}$ AgNO_3 a brick-red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0.001 gm. of NaCl in 50 c.c.

The powder is then squeezed to contain 70–75 per cent. water, and the whole weighed. The quantity Q containing 6.5 grms. dry hide is thus found, weighed out, and added immediately to 100 c.c. of the unfiltered tannin infusion, along with $(26.5 - Q)$ of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, 1 gm. of kaolin added to the filtrate, stirred, and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate are evaporated and reckoned as 50 c.c., or the residue of 50 c.c. is multiplied by $\frac{6}{5}$. The non-tannin filtrate must give no turbidity with a drop of a 1 per cent. gelatine, 10 per cent. salt solution.

¹ Kahlbaum.

(8) *The Analysis of Used Liquors and Spent Tans* shall be made by the same methods as are employed for fresh materials, the liquors or infusions being diluted or concentrated by boiling *in vacuo* or in a vessel so closed as to restrict access of air, until the tanning matter is, if possible, between 3.5 and 4.5 grms. per litre; but if, from any cause, it is impossible to reach this concentration, the weight of hide powder used shall not be varied from 6½ grms. in consequence. The results shall be reported as shown by the direct estimation, but it is desirable that, in addition, efforts shall be made, by determination of acids in the original solution and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder and hence returned as tanning matters. In the case of tans it must be clearly stated in the report whether the calculation is on "the sample with moisture as received or upon some arbitrarily assumed percentage of water; and, in that of liquors, whether the percentage given refers to weight or to grms. per 100 c.c.; and in both cases the specific gravity shall be reported."

The soluble non-tannins obtained by this process are sometimes higher than by the old method, as shown by the following figures:—

	S.N.T. by old method.	S.N.T. by new method.
Sumach No. 1	15.44	17.72
" 2	16.44	18.36
" 3	16.96	19.04

Standard Hide Powder.—H. E. Bennett (*J.S.C.I.*, May 15, 1907) points out the necessity for standardising hide powder. In the past the I.A.L.T.C. have attempted to do this by defining the official powder as that supplied by a certain firm. But this firm was unable to supply a powder continuously satisfying the requirements, thus causing much confusion and variation in results. A better method would have been to define more exactly the term "standard hide powder," and leave members free to obtain it where they liked.

The author is of opinion that the points to which attention must be directed are—

- (1) Texture.
- (2) Acidity.

Texture.—A granular powder gives higher non-tannins than a woolly or fibrous one; but in some solutions, such as quebracho, they do not take up the insoluble matters so readily when the unfiltered tannin solution is used for detannisation. Experience has shown, further, that wet chromed fibrous powders are more convenient to handle than granular ones, and hence the author concludes that the standard powder should be of a fibrous nature. He suggests the following tests:—(1) The appearance of the powder should be fibrous, both to the eye and when examined microscopically, and it should be easily compressible. (2) Separate masses of the powder should adhere when pressed. (3) The powder should not pour from one vessel to another like sand.

Hide powders of identical texture, but varying acidity, gave the following results, showing the importance of a fixed acidity:—

Hide Powder.	Acidity, c.c. $\frac{N}{10}$ HCl 16 grms.	Non-tannins.	
		Oakwood Extract. per cent.	Mimosa D. per cent.
1	12.6	14.5	...
2	6.3	15.6	11.9
3	3.5	18.2	13.4

Acidity.—The same author uses the following test:—A quantity of air-dried hide powder corresponding to 6.5 grms. of hide is digested with 100 c.c. of distilled water, 1 c.c. of phenolphthalein added, and the liquid titrated with decinormal soda (p. 149).

There is no necessity for any considerable amount of acid in a powder which is to be chromed just before use, and the basic chloride method used with the most neutral powder obtainable will detannise any tanning extracts. The author suggests as a limit for acidity an amount of acid per 16.5 grms. equal to not more than 5 c.c. of decinormal alkali. Hide powder conforming with the requirements of the International Association may be obtained through Messrs Portway & Co., or from the "Deutsche Versuchsanstalt für Lederindustrie," Freiberg in Sachsen. Procter and Bennett (*J.S.C.I.*, 1907, 79-80) find that a very satisfactory powder may be made from the hide sawdust produced in the manufacture of pickers from limed buffalo hide. This is heated with acid and washed till free from lime and soluble matter, then dried at a low temperature and ground. It is somewhat granular, but gives higher non-tannins than any other powder, giving complete tannin absorption.

Estimation of Weight-giving Properties of Tanning Materials.—Additional valuable information as to the value of a tanning material may be obtained from the determination of its weight-giving property. This method has been suggested and described by Messrs Gordon Parker and Blockley (*J.S.C.I.*, 1903, 1181), who proceed as follows:—A liquor is made of the tanning material so as to contain not more than 5 per cent. of tannin. This is then analysed by the hide-powder filter method, and such a quantity measured into the flask as, when diluted with water to 500 c.c., would give 500 c.c. of a 5 per cent. solution of tannin. To the strong liquor thus measured out a measured quantity of water is added to make 350 c.c. of solution. Ten grms. of pure air-dry hide powder is then weighed into a bottle of 3 litres capacity and 150 c.c. of water added, and the hide powder and water turned in a churning

apparatus for an hour to soften the powder. Fifty c.c. of 350 of the tanned liquor is now added at intervals of half an hour until all the solution has been employed, the churning of course being continued. There will now, with the 150 c.c. of water used for washing, have been used altogether 500 c.c. of 5 per cent. tannin solution. On completion of the tannage the whole contents of tanned hide powder and liquor are removed to a filter funnel plugged with cotton-wool, the hide powder adhering to the sides of the bottle being carefully rinsed on to the funnel by means of the filtered liquor, no water being used at this stage. When all the hide powder has been removed from the bottle, it is allowed to drain about 24 hours, being occasionally pressed down to squeeze out the liquor which it retains. The whole contents of hide powder are now placed in a weighed basin, and the total weight of wet tanned hide powder noted. After thoroughly mixing, a portion is weighed out to estimate contained water, and a further portion of the wet powder is weighed out, placed in a filter funnel plugged with cotton-wool, and washed with a litre of cold distilled water, in order to remove soluble matter not actually combined with the hide fibres. After being allowed to drain in the funnel for 24 hours, with occasional pressing as before, the total weight of tanned hide is again noted, and a portion weighed out for estimation of water. It is now easy to calculate from these data the actual weight of leather produced under the conditions given.

Colour Measurement.—*The value of tanning materials often depends very much on the paleness of the colour.*

The method recommended by the Association is that a 0.5 per cent. solution of the tanning materials, as estimated by the official method, shall be tinted in a centimetre cell with a Lovibond's tintometer, and the results stated in units of red, blue, and yellow.

It is, however, from an analytical point of view, of little practical value, since the colour greatly depends upon the temperature at which the extract is brought over in the sand-filter method of extraction. Moreover, it varies with standing after extraction. It might be of use to the leather manufacturer to compare the strengths of those solutions which are made by extraction in the cold.

The following is a brief description of the instrument and method of working:—

The tintometer consists of an apparatus for cutting off side lights and giving a direct view of the liquid whose colour is to be estimated, and which is for this purpose placed in a standard cell of definite dimensions which occupies one-half of the field of view. The colour is then matched by a series of standard coloured glasses. The standard glasses are red, yellow, and blue, since by using these three it is possible to make orange, green, and violet, and also to extinguish these colours and thus obtain black. If, for instance, we take equal tints of any two colours, we can produce the intermediate colours, for example, five red units and five yellow

units give five orange units, or five red and five blue units give five violet, or five of all three colours absorb five units of light, giving five units of black or neutral tint. Fig. 29 shows the instrument generally used. The liquor when tested is placed in a one-inch or half-inch cell in the left-hand compartment, and the standard glasses are adjusted in the right-hand compartment, until the two colours exactly match when viewed through the eye-piece; when this occurs the visual composition of the light coming through each half of the instrument will be the same. It is best to work in a room illuminated by a north light, and if surrounding objects obstruct the light it is advisable to cover the window which illuminates the surface with pure white tissue paper. Having thus obtained an even, colourless illumination of the white surface, the whole

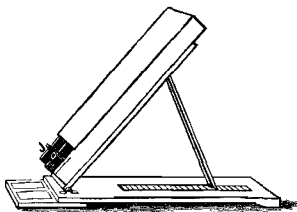


FIG. 29.

apparatus must be arranged so that the illumination of the two halves is the same. To test this, two glasses of the same colour and equal denomination are taken, and one is placed in each compartment and viewed through the eye-piece. If the illumination is not equal the colours will appear unequal, and the apparatus must be moved until they exactly match each other. Either reflected or direct light may be used, but never changed, as the results given are not the same with both, but are always constant for each kind of light. Artificial light, with the exception of the Nernst electric lamp, is inadmissible.

Although the standards are purely arbitrary, they are rigidly fixed, the unit of each colour being derived from a definite pure chemical substance which can be reproduced with exactness. The units having been fixed, the scales become quantitative; they are so divided that the eye can easily distinguish between the colour value of two successive glasses, and the effects are cumulative. For tanning liquors a half-inch cell is generally used, but other sizes, varying from $\frac{1}{16}$ th inch upwards, may be obtained. To make a colour measurement, the cell is filled with the liquid and placed in one compartment of the apparatus, and the three colours are arranged in the other compartment, till when viewed through the eye-piece an exact match is obtained. The results are then tabulated accord-

ing to the visual sensations they produce. The following example will illustrate this:—

Suppose the standard glasses used were—

Red 2.7 Yellow 0.5 Blue 1.5.

Now 0.5 unit of yellow will, if superimposed upon 0.5 of blue and red, quench 0.5 unit of light, *i.e.* produce 0.5 unit of black. Hence we have this amount of black as a component part of the colour. We have left 1.0 of blue and 2.2 of red. Now 1.0 of blue together with 1.0 of red will give 1 unit of orange, and leave us with 1.2 of free red. Hence the visual composition is—

Black 0.5 Orange 1.0 Red 1.2.

The following table (XL.) gives several examples which may be made use of for checking the method of working.

TABLE XL.

Substance Examined.	Light brighter than standards.	Standard Glasses used.			Visual Colour.		
		Red.	Yellow.	Blue.			
1. Cobalt sulphate 1 per cent. sol.,	..	3.7	.46	.07 =	Black .07	Orange .39	Red 3.24
2. Potassium ferrocyanide 10 per cent. sol.,	..	0	3.9	.25 =	Green .25	Yellow 3.65	..
3. Water, 3-feet strata,	..	1.9	3.3	1.9 =	Black 1.9	Yellow 1.4	..
4. Green glass,	..	0	25	.12 =	Black .12	Orange .13	Yellow ..
5. Yellow glass,	5.12	.2 =	Black .2	Orange .45	Yellow .7
6. Claret glass,	..	20	3.1	5.8 =	Black 2.1	Violet 2.7	Red 14.2
7. Emerald green in powder,	2.4	0	13.5	13.5 =	Light 2.4	Green 13.5	..
8. Prussian blue in powder,	..	9.0	1.0	6.8 =	Black 1	Red 2.2	Violet 5.8
9. White lead in powder,	..	.08	.15	.2 =	Black .08	Green .07	Blue .5

CHAPTER X.

COMMON VEGETABLE TANNINS.

A FEW of the more important tanning materials require special notice, but the analysis of the majority calls for no special comment; for particulars as to their origin and tannin-content Procter's *Principles of Leather Manufacture* should be consulted.

Sumach.—This material is perhaps most important of the vegetable tannins, and owing to the fact that it is almost entirely used in the ground state is subject to considerable adulteration. There are many different kinds of sumach, of which the Sicilian variety (*Rhus Coriaria*) is the most valuable.

The sumach plant is a shrubby bush, the leaves and smaller branches of which contain large quantities of tannin.

The plants are propagated by suckers from older plants, which are planted in the spring and pruned to 6 or 8 in. The younger bushes, which begin to bear a year after planting, do not yield such large amounts of tannin as the more mature plants. The leaves, having been gathered, are dried in the open air, or on covered threshing floors. They are then well beaten in order to remove the stems, and the leaves are exported in this state as "leaf" or "baling" sumach. But the bulk is ground to a velvety powder of yellowish green colour, and is then "ventilated" in order to remove sand and iron.

The ventilation is a very important process and is frequently not properly carried out. Insufficient ventilation is detected by a high ash containing silica and frequently particles of metallic iron or magnetic oxide. The presence of the latter is especially objectionable, since they cause stains on goods.

Good varieties of sumach contain 25–30 per cent. of tannin, and, in exceptional cases, 31 per cent.

There are several varieties of American sumachs, namely, *R. glabra*, *R. copallina*, *R. cotonoides*, *R. typhina*, *R. metopium*, and *R. aromatica*.

R. glabra is largely grown in the southern states, U.S.A., where it thrives remarkably well. It is used in the place of Sicilian sumach. Leathers tanned by it are of a darker colour than those treated with Sicilian sumach. It contains from 20–25 per cent. of tannin.

R. copallina is somewhat similar to *R. glabra*, and the percentage of tannin is, if anything, slightly lower.

R. rotundoides contains about 20 per cent. tanning matter.

The percentage of tannin in the other varieties varies from 8-16 per cent.

R. toxicodendron, the "poison ivy," is a climbing plant, and causes severe irritating eruptions when handled.

Procter gives the following account of sumach cultivation in Virginia. The leaves are collected and carried by the country people and sold and delivered to owners of mills for grinding. Since their particular object is to secure the largest possible quantity of the product at the lowest cost, little attention is paid to the quality obtained or the method of collecting.

Buyers of sumach leaves for grinding depend largely upon colour for determination of value. The leaves when ready for market should present a bright green colour, which is evidence that they have suffered neither from rain after being gathered, nor from heating during the process of drying. Leaves having a mouldy odour or appearance are rejected.

Analysis of Sumach.—In addition to the determinations of tannins and non-tannins, an analysis of sumach should always include moisture, ash, silica, free and combined iron, together with a microscopical examination of the sample.

Sicilian Sumach and its Adulterants.—According to Andreasch (*J.S.C.I.*, 1898, 775 and 933) the modes of adulteration may be divided into two classes:

- (1) Adulteration by mixing the stems with the leaf, sumach which has been spoilt during harvesting, by rain or otherwise, also by admixture of other tanning materials in ground form.
- (2) The adulteration of sumach by foreign materials. Merchants often add large quantities of sand of a special yellow colour. Sumach which has been already used in the tan-yard is often bought back, dried and ground in with a good sample. The most frequent adulterants are the leaves of the *Cistus salvifolius*, fig leaves (*Ficus carica*), vine leaves, *Ailantus glandulosa*, *Pistacia lentiscus*, and *Tamarix Africana*.

The last two are the most frequent adulterants.

The adulteration of sumach by pistacia has very largely increased of late years, owing to the difficulty of its detection without the aid of a microscope, and the Sicilian growers blame the merchants for causing this state of affairs by continually demanding a low-priced sumach.

According to Andreasch, sumach proper should contain from 24-30 per cent. tannin. When mixed with stems, leaf veins, etc., the percentage drops considerably, as is shown in the following table:—

TABLE XLI.

	Tannin.	Non-Tannins.
Dry raw material,	20.70	19.11
After winnowing,	19.00	16.70
After ventilation,	24.91	15.75
After first grinding,	24.28	16.67
After ventilation and second grinding	25.82	16.48
After first grinding,	27.28	16.11
After ventilation and second grinding	29.98	16.44
Stems and leaf-veins only,	14.70	11.70
Stems and leaf-veins only,	8.20	14.43
Stems and leaf-veins only,	11.53	17.77
Sumach leaf, parenchyma only,	23.41	17.17
Sumach leaf, parenchyma only,	29.45	15.89

Of course, the amount of stems and leaf-veins which remain in the sumach after winnowing depends upon the care with which that operation has been carried out. Sicilian sumach should never contain less than 25 per cent. of tanning matter removable by hide powder, nor more than 18 or 19 per cent. of soluble non-tannins. The figures for some of the commoner adulterants are:—

	Tannins, per cent.	Non-Tannins, per cent.
<i>Pistacia lentiscus</i> contains	13-17	20-22
<i>Tamarix</i> contains	8.3-9.7	23-26
<i>Ailantus</i> „	10	17.5

Hence, if the non-tannins in a sample of sumach exceed 20 per cent., the presence of an adulterant may be safely assumed.

The following qualitative chemical tests for sumach are recommended by Andreasch:—

Digest 20 grms. of the material in a litre of water at 60° C. and filter. If *Pistacia* be present, the addition of two or three drops of 40 per cent. formaldehyde gives, in a neutral solution, a light yellow flocculent precipitate insoluble in cold water, while with a pure sumach no change occurs. If the material is chiefly genuine sumach, a yellowish cloud appears, which comes down after a few days as a precipitate. The precipitate (in the case of *pistacia*, is of a gelatinous character, and could not be mistaken for the precipitates caused by old sumach which has fermented, or *tamarix*, which has somewhat the same colour but is not gelatinous. A solution of arsenious acid, when warmed with a solution of *pistacia*, gives a white powdery precipitate. Mercurous nitrate produces an egg-yellow precipitate, which turns to olive-green, and finally to a dark green, the rapidity of the colour-change depending upon the quantities of *pistacia* in solution.

Detection of Tamarix.—Sulphurous acid produces a cloudiness and finally a precipitate. Potassium cyanide gives a flocculent, dirty yellow precipitate; but neither of these reagents reacts with genuine sumach.

Bromine-Water Test.—Since sumach contains only pyrogallol-tannins, while most of its adulterants contain catechol-tannins, it follows that an extract of sumach should give no precipitate with bromine-water. A sumach that gives any turbidity with bromine is always to be regarded with suspicion.

Sulphuric Acid Test.—If an alcoholic extract of a catechol-tannin be carefully poured upon the surface of strong sulphuric acid in a test-tube, a crimson ring is formed at the junction of the two liquids, while with pyrogallol-tannins a yellow or brown colour is produced.

Lime-Water Test.—If one-fifth normal lime-water, used as in Parker and Payne's collin method, be added to excess of the filtered aqueous extract, a pure sumach gives an immediate yellow colour, which ultimately changes to a bright green; while an adulterated sample containing pistacia or lentiscus usually gives a final brown or reddish-brown colour. The following are a few of the characteristic tints:—

Mangrove,	deep red.
Mimosa,	lavender colour.
Myrabolans,	brown-yellow.
Chestnut,	mahogany.

All pyrocatechol tannins give a precipitate with diazobenzine chloride ($\frac{1}{2}$ per cent. solution), while pyrogallol tannins do not (Nierenstein and Webster, *Collegium*, 1907, 244). Hence any sumach which gives a positive reaction with this reagent must be adulterated.

The process may be made quantitative by filtering off the precipitate and determining its nitrogen content, an allowance of 0014 grm. being made for the 2.5 grms. of the sample used, this being the average given by a pure sumach. Fifty c.c. of a 5 per cent. solution are treated with 10 c.c. of a 2 per cent. solution of the diazo-benzole-chloride, and allowed to stand over night. The precipitate is then filtered and washed with hydrochloric acid and then distilled water, and the paper and precipitate kjeldahled. The diazo-benzole-chloride solution may be prepared by passing the fumes from a mixture of nitric acid and arsenious oxide through a 2 per cent. solution of aniline hydrochloride until, after allowing to stand for ten minutes, there is just a trace of free nitrous acid present (tested for by iodised starch paper).

O'Callaghan and Randall (*J.S.C.I.*, 1899, 105) give the following qualitative tests for sumach, tamarix, and pistacia.

“Twenty grms. of the sumach to be tested are extracted with about a litre of water at 70° C., or the ordinary solution prepared for analysis may be used. The liquor must be filtered until perfectly clear. Good results may be obtained by taking 20–50 c.c., and the work may be done in test-tubes or glasses. The strength of the reagents used should be about 5 per cent., of which about five drops may be added to give the reaction. The following are the reactions in tabular form:—

TABLE XLII.

Reagent.	Sumach.	Pistacia.	Tamarix.
Mercurous nitrate.	Yellow precipitate, turning to greenish black.	Dirty white precipitate, turning to greenish-black. Cloudiness, finally a pinkish precipitate.	Dirty white precipitate, turning to greenish-black. Cloudiness, finally a pinkish precipitate.
Sulphurous acid.	No reaction.	White precipitate.	No reaction.
Ammonium chloride	No reaction.	White-yellow precipitate.	No reaction.
Ammonium bromide.	No reaction.	No reaction.	Dark olive-green precipitate.
Potassium chromate.	No reaction, darkening of colour.	darkening of colour.	Deep yellow flocculent precipitate.
Potassium cyanide.	No reaction.	No reaction.	White precipitate.
Oxalic acid.	No reaction.	White precipitate.	White precipitate.
Boiling with nitric acid.	Yellow colour.	Red-brown colour.	No effect.

Of the above reagents, mercurous nitrate, sulphurous acid, and potassium cyanide are quoted by Andreasch. The new reagents are ammonium chloride, potassium chromate, and oxalic acid.

E. Scarlata (*Analyst*, 1906, 221) gives the following method of detecting the presence of tamarix and lentiscus in sumach, depending upon the relative specific gravities of the leaves. If powdered sumach be allowed to fall upon glycerine (sp. gr. 1.26), which is then brought to the boiling-point and allowed to stand for an hour, the sumach sinks and the supernatant liquid assumes a greenish-yellow tint. Lentiscus floats on the surface and produces a wine-red coloration, while tamarix remains in suspension, settling only after 24 hours. Five grms. of the sample are passed through a sieve and introduced into a test-tube containing 110 c.c. of glycerine. The liquid is heated to boiling-point without shaking, and boiled for a few moments until complete emulsion takes place. If after 24 hours leaves still float on the surface and the glycerine is reddish in colour, the presence of lentiscus is certain. If, after 2 hours, part of the powder is still in suspension, the presence of tamarix is probable.

While chemical tests will give, in many cases, evidence of adulteration, they are of little value in comparison with a microscopical examination; and this should be carefully carried out in every suspicious case. Much work has been done on this subject by Andreasch and others, and recently by Messrs Lamb and Harrison, Procter and Priestman, the results of whose work will be briefly described.

Microscopic Examination of Sumach.—Lamb (*J.S.C.I.*, 1899, 403) states that the most common adulterants of sumach are *Coriaria myrtifolia*,

Vitis vinifera, *Ailantus glandulosa*, *Pistacia lentiscus*, and *Tamariz Africana*. The last two are the most usual adulterants, and both are grown in most places where sumach is obtained. The author found that it is possible to identify all the common adulterants of sumach by means of a microscopical examination of the cuticles, the appearance of the lower cuticle being generally sufficient to demonstrate the presence of adulterants. To prepare the cuticles, the leaves were powdered with moderately dilute nitric acid, and subsequently washed and stained with an aniline dye and examined. In sumach it was, however, found necessary to previously boil the leaf with a 10 per cent. solution of caustic soda. The chief characteristics of the cuticles of sumach are given as follows:—

Rhus coriaria.—On lower cuticle long thin hairs and small club-shaped hairs; the cells at the base of the latter are triangular, and radiate from the point of union of the hair and epidermis. The stomata are small in size and few in number; they are oval in shape and rather indistinct. The upper cuticle contains no stomata; it has a number of long thin hairs and a few club-shaped hairs; the majority of the cells are either pentagonal or hexagonal in shape.

Rhus cotinus (Venetian sumach).—This is the sumach chiefly used in dyeing, and is much weaker in tanning matter than *R. coriaria*. The cuticle has no long hairs, and the cells are very irregular, both in shape and size; in other respects the cuticle resembles that of Sicilian sumach.

Rhus glabra.—This American variety of sumach can hardly be classed as an adulterant; it contains more than 26 per cent. of tanning matter. The cuticle has a large number of club-shaped hairs, but no long thin hairs. The stomata are small, numerous, and distinct; the cells are polygonal in shape.

Rhus metopium.—The cuticle has no hairs; the stomata are large, numerous, and distinct; the cells are irregular in shape, and appear arranged in circles with stomata as centres.

Pistacia lentiscus.—This plant is commonly known as the "schina" or "skens," and is the chief adulterant of sumach. The lower cuticle possesses no hairs; the stomata are large and more broadly oval than those of sumach. The cells are small and very irregular in shape. The cuticle can be readily found, if present, in ground sumach, by boiling with strong nitric acid, when most of the sumach is destroyed, leaving chiefly the adulterant.

Tamariz Africana.—The leaves are extremely small; the cuticle consists of a number of quadrilateral cells, irregular in size. The stomata are very small and indistinct, and there are no hairs.

Coriaria myrtifolia (French sumach).—The cuticle possesses large irregular-sided cells, and the chief peculiarity is a large cell entirely surrounding the stomata. There are also peculiar markings on the surface of the cells.

Ailanthus glandulosa.—The cells in this cuticle are small, and have the appearance of a fine and intricate network; the stomata are large and distinct; there are no hairs.

Vitis vinifera (grape-vine).—The hairs are very long, forming a kind of matted layer on the outside of the cuticle; they are very similar to cotton fibres. The stomata vary greatly in size; the cells are polygonal, approximating to hexagons; but they are very indistinct.

Ostrya compressa (*Fusanus compressus*, *Colpoon compressum*, *Thesium colpoon*), known commercially as Cape sumach.—Its tanning properties are very similar to those of Sicilian sumach. The cells in the cuticle are approximately hexagonal in shape, and smaller in size than those of *Coriaria myrtifolia*. The stomata are very large and distinct, the guard cells showing remarkably well.

Arctostaphylos (*Arbutus uva ursi*) (bearberry).—The cuticle is characterised by its bold, irregular, medium-sized cells, approximately polygonal in shape; the stomata are moderately large, and very irregularly distributed over the surface; the guard cells are large and distinct.

In a further paper by M. C. Lamb (*J. Soc. Dyers and Colourists*, 1904, 265; and *J.S.C.I.*, 1905, 46), a method for the examination in powder form is given.

One or two grms. of the sample to be tested are heated with nitric acid (1 : 1) until nitrous acid fumes are evolved, the mixture is allowed to stand for 15 to 30 minutes, and then again heated until the solution becomes clear. The liquid is diluted and filtered; the small particles of leaf cuticle remaining on the filter are removed and coloured by treatment with a weak solution of some suitable dyestuff, e.g., Bismarck brown, safranin, methylene green. The dyed particles are washed and afterwards transferred to a glass slip for microscopical examination. By treatment with nitric acid, pure sumach almost completely dissolves, leaving a sumach "wreck"; the adulterants, however, are unaffected by the treatment.

Illustrations taken from photomicrographs of samples of ground sumach adulterated with the two most common adulterants, *Pistacia lentiscus* and *Tamarix Africana*, are shown in the paper; no hairs appear on the cuticles of either of these leaves. The stomata of the lower cuticle of *Pistacia lentiscus* are larger and more numerous than those of sumach, whilst the cells are nearly all hexagonal in shape. *Tamarix Africana* leaves possess polygonal cells and very few stomata.

A "sumach" tanned leather may sometimes be examined for adulteration with pistacia or tamarix by the same method, the leather during the tanning usually becoming impregnated with minute particles of the sumach and adulterants. The leather is first dissolved in caustic soda, and the cuticles prepared by treatment with nitric acid in the same manner as when dealing with sumach.

According to H. Priestman (*J.S.C.I.*, 1905, 231), genuine sumach is

easy to distinguish from all other vegetable products used as adulterants, because both upper and lower cuticles are covered with a dense growth of hairs. Those of the upper surface taper from root to point, the root itself being bulbous, so that each hair resembles a hob-nail in size and shape when seen in an enlargement of 120 diameters. The upper cuticle is stronger than the lower one, and, when separated from the vein structure, shows well-defined cells so arranged that the base of each hair forms the centre of a symmetrical group of ten or eleven four-, five-, or six-sided cells. Stomata proper seldom occur on the upper cuticle. The lower cuticle is very thin and transparent, but is also covered with hairs of from 0.45 to 0.3 inch in length. The same author has studied the conditions under which the cuticles of sumach and some of its adulterants separate when immersed in pure nitric acid. The following table shows the results of these tests:—

TABLE XLIII.

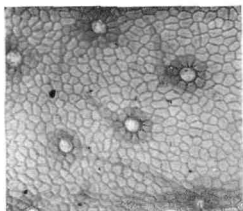
	Cuticles separate at	Totally dissolved at
<i>Rhus coriaria</i> leaves, . . .	60°-65° in 10 mins.	98° in 15 mins. from cold.
" " stems, . . .	75° " " "	95°-98° " " "
<i>Tamarix</i> stems, . . .	80° " " "	90° " " "
<i>Pistacia lentiscus</i> , . . .	65° " " "	98° " 20 " "
<i>Coriaria myrtifolia</i> , . . .	75° " " "	98° " 20 " "
<i>Rhus metopium</i> , . . .	70° " 15 " "	95° " 25 " "
<i>Rhus glabra</i> , . . .	75° " 15 " "	Insol.
<i>Colpoon compressum</i> (<i>Oxyris compressa</i>), . . .	50° " 15 " "	98° " 25 " "
<i>Atlantus glandulosa</i> , . . .	75° " 15 " "	Insol.

This method may be used for preparing the cuticles for microscopic investigation. The cuticles are very characteristic, as will be seen from the accompanying reproductions from photographs¹ (fig. 30), taken from the same paper.

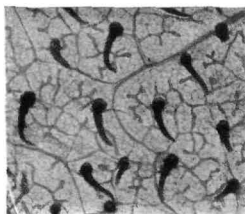
The Mineral Constituents of Sumach.—While the most important point in a sumach is undoubtedly the percentage of tannin, the mineral constituents should not be overlooked; and a sumach with an ash of over 6 per cent. should undoubtedly be considered adulterated. The same remark applies to the presence of more than 0.1 per cent. of combined iron, while only traces of free iron (0.001 per cent.) should be permitted, as much damage may be done through the presence of this substance. In a recent paper (*J.S.C.I.*, 1904, 1137), it was suggested by the author that the following standard should be laid down:—

Ash,	6.5 per cent.
Silica,	0.75 "
Iron,	0.15 "

¹ Lent by the Society of Chemical Industry.



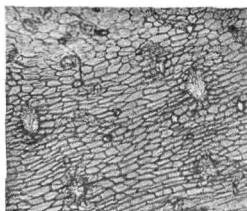
1.—*Rhus coriaria*, upper. $\times 84$.



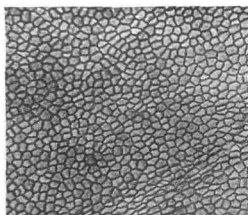
2.—*Rhus coriaria*, upper, aged. $\times 84$.



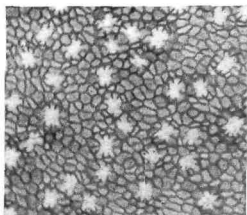
3.—*Rhus coriaria*, lower. $\times 84$.



4.—*Rhus coriaria*, stem cuticle. $\times 84$.

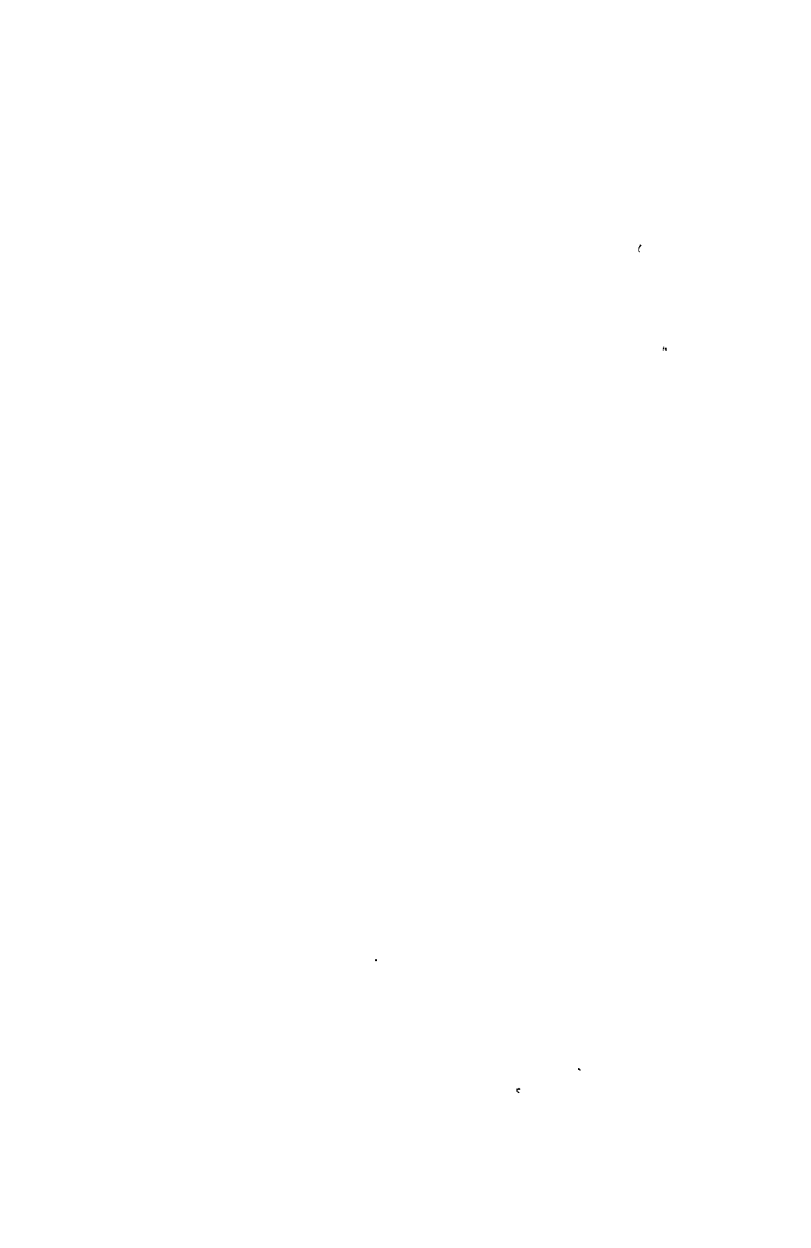


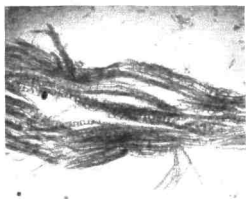
5.—*Pistacia lentiscus*, upper. $\times 84$.



6.—*Pistacia lentiscus*, lower. $\times 84$.

FIG. 30.—CUTICLE OF PLANTS.

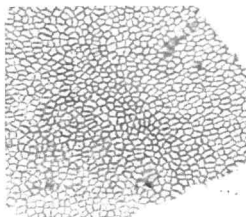




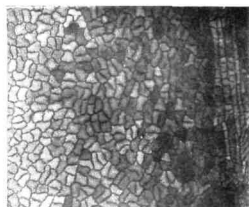
7.—*Tamarix*, stem substance. $\times 42$.



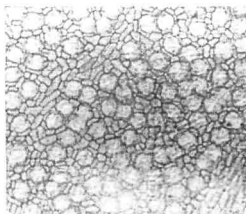
8.—*Tamarix*, stem cuticle. $\times 84$.



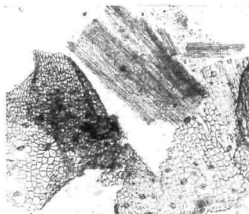
9.—*Caroubier*, upper. $\times 84$.



10.—*Rhus metopium*, upper. $\times 84$.

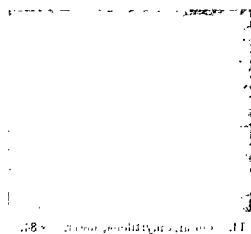


11.—*Rhus metopium*, lower. $\times 84$.

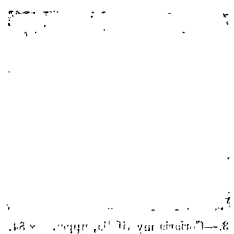


12.—*Arboisier* substance and cuticle. $\times 42$.

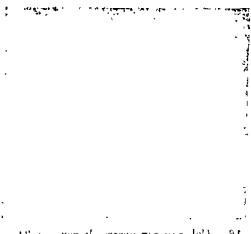
FIG. 30.—CUTICLE OF PLANTS.



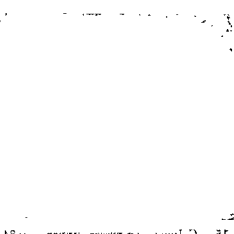
11 - *Micrograph showing a dark, rectangular field.*



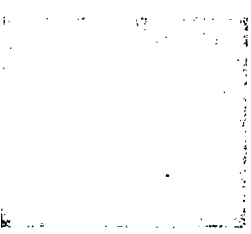
12 - *Micrograph showing a dark, rectangular field.*



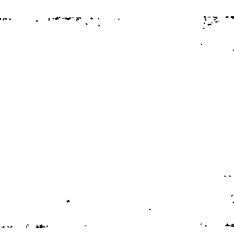
13 - *Micrograph showing a dark, rectangular field.*



14 - *Micrograph showing a dark, rectangular field.*

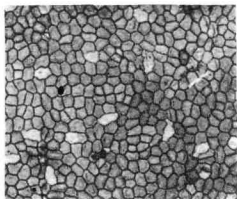


15 - *Micrograph showing a dark, rectangular field.*

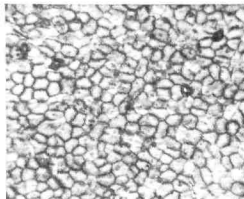


16 - *Micrograph showing a dark, rectangular field.*

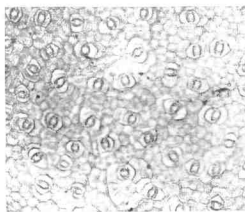
Fig. 11 - 16 - *Series of plates.*



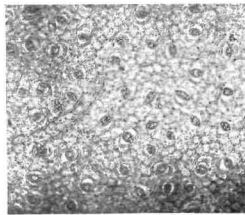
13.—*Coriaria myrtifolia*, upper. $\times 84$.



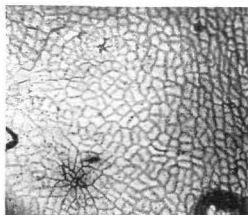
14.—*Coriaria myrtifolia*, lower. $\times 84$.



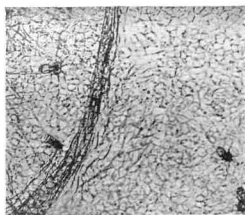
15.—*Colpoon compressa*, upper. $\times 84$.



16.—*Colpoon compressa*, lower. $\times 84$.

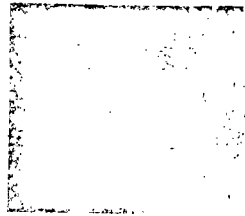


17.—*Rhus cotinus*, upper. $\times 84$.

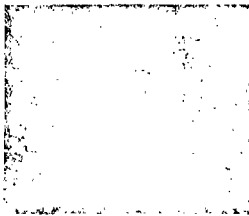


18.—*Rhus cotinus*, lower. $\times 84$.

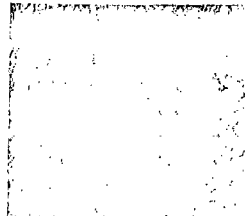
FIG. 30.—CUTICLE OF PLANTS.



18—*Alisma* (upper) spores. $\times 81$.



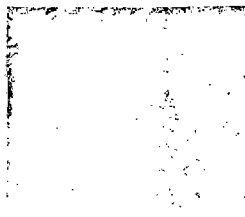
19—*Alisma* (lower) spores. $\times 81$.



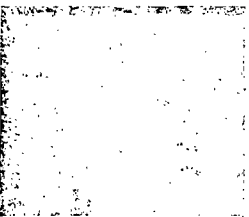
20—*Thlaspi* spores. $\times 81$.



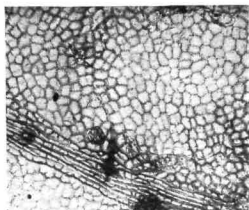
21—*Thlaspi* spores. $\times 81$.



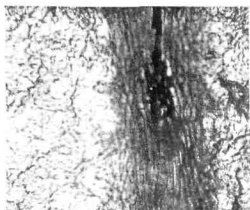
22—*Vitis* (upper) spores. $\times 81$.



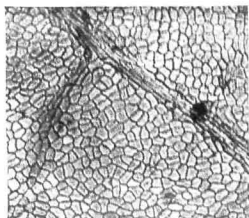
23—*Vitis* (lower) spores. $\times 81$.



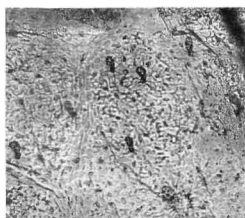
19.—*Ailantus glandulosa*, upper. $\times 84$.



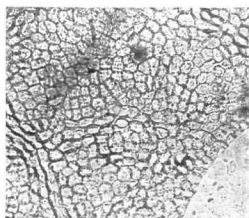
20.—*Ailantus glandulosa*, lower. $\times 84$.



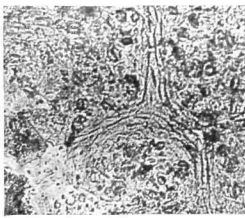
21.—*Rhus glabra*, upper. $\times 84$.



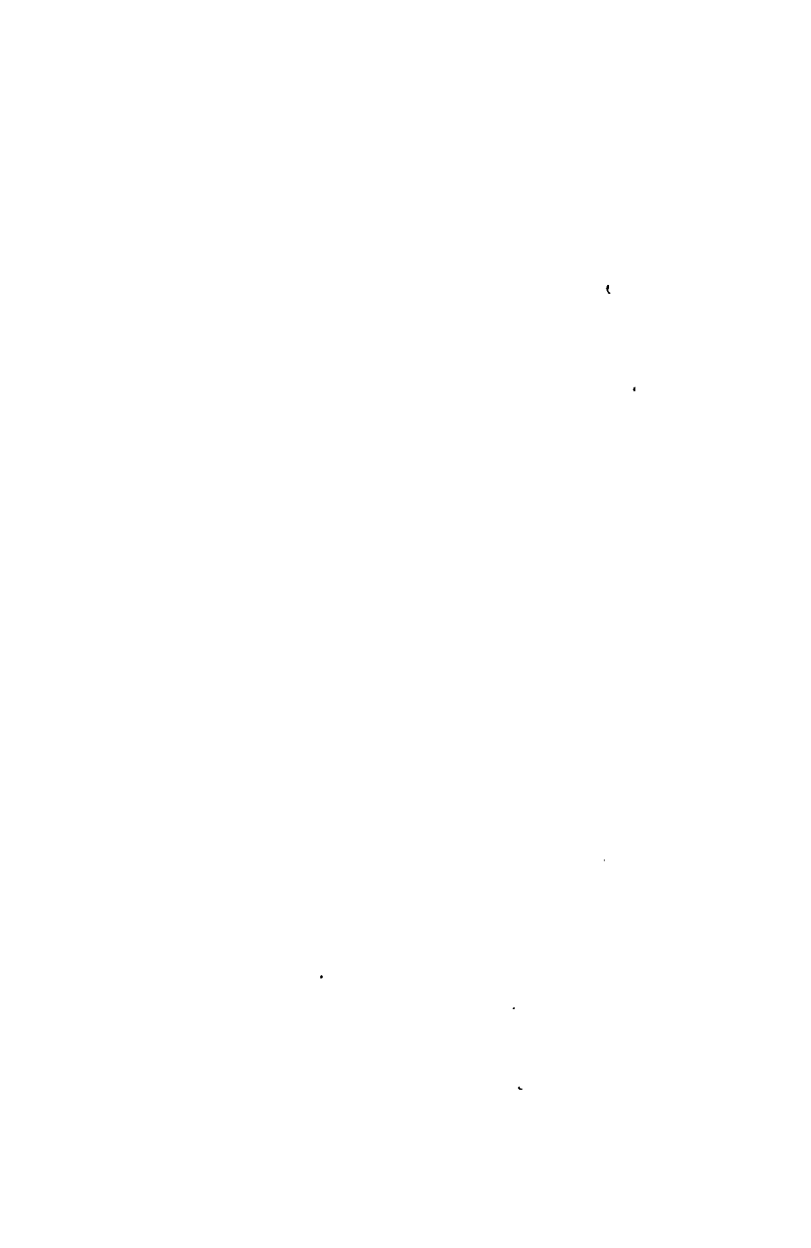
22.—*Rhus glabra*, lower. $\times 84$.



23.—*Vitis vinifera*, upper. $\times 84$.



24.—*Vitis vinifera*, lower. $\times 84$.



These figures were arrived at by taking a large number of commercial sumachs, subjecting them to a process of winnowing, and determining the ash before and after the operation.

In no case was the percentage of the ash greater than 6.5. The presence of an undue proportion of leaf-stem will not materially increase the ash, although, if the stalks be left in, the ash will often be somewhat high. The following determinations were made by M. C. Lamb upon a sample of pure sumach:—

	Percentage amount of sample.
Parenchyma of leaves,	72.5
Leaf, mid-rib,	6.6
Stalks,	20.9

This illustrates the large proportion of stalks which are sometimes sold to the grinder.

Ash determinations of the above give the following results:—

Parenchyma of leaves,	6.3	per cent.
Leaf-stems,	8.1	"
Stalks,	3.9	"
Sample as a whole,	5.89	"

According to the same author, the average percentage of ash found in three samples of ground tamarix was 10.0, and in three samples of ground lentiscous, 6.8.

Detection of Iron in Sumach.—Metallic iron or magnetic iron oxide can readily be detected by stirring an ounce or two with a magnet. A small electro-magnet answers the purpose admirably, since the particles can be subsequently easily removed by stopping the current, and weighed. More than a trace of magnetic iron is a certain sign of insufficient ventilation. The presence of iron is a frequent cause of stains, since it forms tannate or gallate on the skins. If it is desired to separate free from combined iron, the total iron is determined in one part of the sample, and a second portion well stirred with a magnet, and the iron afterwards redetermined. Or the iron removed by the magnet may be dissolved in nitric acid and estimated colorimetrically by means of potassium ferrocyanide. The percentage of iron present will generally be too small to weigh. The following is a good qualitative method of examining sumach for iron in the absence of a magnet (Becker, *Collegium*, 1905, 373):—Two glass plates are covered with pieces of filter paper, one of which has been treated with a dilute tannin solution. About 1 grm. of the finely-powdered sumach is evenly spread over this plate. The second plate, to which is attached a filter paper treated with acetic acid, is now pressed down on the first, when, in the presence of iron, small black spots due to tannate will make their appearance on the first paper.

A. Turnbull determines the degree of *Ventilation* in a sumach as follows:—

A weighed quantity is incinerated, the ash treated with hydrochloric acid, and the residue (siliceous sand) filtered, washed, and digested over night with warm saturated carbonate of soda solution. The residue of sand is then filtered off, washed, ignited, and weighed. Well-ventilated sumachs, when treated in this way, show less than 1 per cent. of sand, moderately ventilated samples $1\frac{1}{2}$, and bad samples 2 per cent. and over. The latter should be rejected.

Tamarix (*Tamariscina*).—There are two or three varieties of tamarix, but the only one much used is *Tamarix Africana*, which consists of ground twigs containing about 9 per cent. of tannin, and very highly soluble non-tannins, 20 to 26 per cent.

Commercial tamarix frequently contains much sand, and is distinguished from many other similar tanning materials by its high nitrogen content. The leaves of tamarix on grinding give a light green or yellow powder.

Pistacia.—*Pistacia lentiscus* consists chiefly of a ground leaf. It is grown chiefly in Sicily, Cyprus, and Algeria, and contains about 14 per cent. of catechol tannins. It darkens on exposure to light, as also does the leather made from it. It contains from 16 to 20 per cent. of soluble non-tannins. Both the upper and lower cuticles are considerably thicker than those of sumach and readily separate in pure nitric acid at 65° C. (Priestman, *loc. cit.*), and remain undissolved for a few minutes longer than those of sumach at the boiling point. The cuticle is very characteristic, being only slightly distorted or elongated over the stems. The upper cuticle seldom contains stomata, but they are very frequent in the lower, occurring as often as nine or ten times in every one-hundredth of a square inch. Priestman says that "both upper and lower cuticles are devoid of fibre. Both show very distinct cells, very regularly disposed." The leaves are of a dark green colour with a feathery feel, and when ground possess a sharp penetrating smell.

Myrobalans.—Myrobalans is the trade name given to the dried fruit of various species of Indian *Terminalia*, the chief source being the *Terminalia chebula*, a tree 40 or 50 ft. high and valuable also for its timber. The nuts are about the size of a pigeon's egg, and may be either round and smooth or oblong and wrinkled. There are five chief varieties, named after the district from which they come, and the price and value vary considerably. Moreover, it is very difficult, if not impossible, to tell by inspection which are the richest in tannins. Parker and Blockey (*Collegium*, 1904, 101) have shown that often the hand-picked varieties, which fetch a higher price on the market, actually contain less tannins than the cheaper varieties, proving that the colour of the fruit is no indication of value. It appears that the picked varieties are taken from the trees before the sun has had time to darken the colour, and finally the trees are shaken and the fruit collected and again picked over, being sorted into three kinds accord-

ing to colour only. The same authors have found that the hand-picked samples are not only poorer in tannins, but give darker solutions and leather of a darker colour than the riper fruits, the best samples being those that were left on the trees the longest. Table XLIV. (p. 167) shows the results of analyses of the different varieties.

Myrobalans should be tested for bloom by the process described under valonia, since its power of forming bloom is one of its chief properties. According to Parker and Blockey (*loc. cit.*), 100 lbs. of myrobalans will yield from 5 to 20 lbs. of bloom, according to the variety.

TABLE XLIV.

Analyses and Tintometer Readings recalculated at 12 per cent. of Water.

	Tannin.	Non-Tannins.	In-soluble.	Water.	Tintometer Colour Measurements of Solution containing 0.5 per cent. of Tannin measured in 1 cm. Cell.		
					Red.	Yellow.	Black.
Picked Bhimley,	33.0	13.1	41.7	12.0	0.8	2.5	...
Bhimley 1,	38.4	16.1	33.5	12.0	0.3	1.8	...
Bhimley 2,	35.2	14.2	38.6	12.0	1.0	5.1	...
Picked Rajpore,	32.2	13.0	42.8	12.0	1.1	3.0	...
Rajpore 1,	35.4	12.1	40.5	12.0	0.9	4.0	0.1
Rajpore 2,	27.6	12.7	47.7	12.0	2.5	7.4	...
Picked Jubblepore,	28.9	12.7	46.4	12.0	0.8	2.2	...
Jubblepore 1,	36.5	14.4	37.1	12.0	0.8	3.4	...
Jubblepore 2,	27.3	14.1	46.6	12.0	1.3	5.9	...
Vingorlas 1,	31.5	9.5	47.0	12.0	1.2	3.0	...
Fair Coast Madras,	34.8	15.4	37.8	12.0	1.2	3.9	...

Valonia is the trade name of the acorn cup of the Turkish oak (*Quercus Egilops*). It is grown chiefly in Asia Minor, although a poorer quality comes from the islands of the Grecian Archipelago and is known as Greek valonia, the other variety being in contradistinction termed Smyrna valonia, from its port of shipment. The difference between the two varieties is shown by the following figures representing analyses made by Messrs Parker and Leech (*J.S.C.I.*, 1903, p. 1185).

TABLE XLV.

	Tannin.	Non-Tannins.	Insoluble.	Water.
Smyrna valonia,	32.43	12.50	43.07	12.00
" cup,	30.99	12.79	44.12	12.10
" beard,	43.61	14.45	29.93	12.01
Greek valonia,	32.07	12.96	42.87	12.00
" cup,	27.37	12.92	47.71	12.00
" beard,	41.03	13.96	33.01	12.00

A very important consideration where valonia is used is the amount of bloom, *i.e.* ellagic acid, which it deposits, since no doubt the chief value of valonia is the power which it possesses of depositing ellagic acid from its solutions. Bloom is measured by Messrs Parker and Leech in the following way: 500 grms. of the finely-ground sample is placed in a beaker and extracted with boiling water until a liquor of 45° Bk. is obtained.

A litre of the clear liquor is then put into a large beaker and allowed to stand for 13 days, after which the precipitated ellagic acid is filtered off, washed, dried, and weighed. The liquor is then allowed to stand for two further periods of 13 days, the precipitate being again weighed after each interval. Ellagic acid is insoluble in water. The *acid-forming* power of valonia is estimated by extracting 100 grms. of the ground substance with 500 c.c. of water for some hours at a temperature of 80° C., after which it is filtered and titrated with lime water.

Quebracho.—*Quebracho Colorado* contains from 17 to 20 per cent. of tannin, which is of a red colour and difficultly soluble. There is a catechin present, and fustin, a colouring matter, which is identical with that of "young fustic." Some of the colouring matters present are very difficult to separate, and so cause much annoyance in practice, as they impart a disagreeable red colour to the leather.

When quebracho wood is ground, it rapidly loses its tannin on exposure to air. The bark of the wood, which contains about 13 per cent. of tannin, does not tan.

On account of the large quantity of difficultly soluble tannins present in quebracho, the liquors made from its extracts generally turn turbid on cooling. This difficulty has been overcome by heating the extracts in closed vessels with bisulphites, sulphites, sulphides, and caustic alkalis, the products being known as "soluble quebracho extract," and sold as such. The tannins present probably form compounds with the alkaline sulphites, setting free the sulphurous acid and combining with the base. However, in the course of manufacture the greater part of the sulphur dioxide escapes, leaving the extracts alkaline, or neutral.

The analysis of quebracho includes the usual determinations, and great care should be taken to work with liquids containing the correct amount of tannin, since in stronger solutions the results obtained by the hide-powder filter differ considerably from those obtained with dilute solutions, the powder appearing to have the power of absorbing larger quantities of soluble non-tannins from concentrated solutions. It has already been mentioned that if a sulphited extract be treated with a neutral hide powder a part of the tannin, namely that combined with the alkali, is not absorbed. This difficulty may be overcome by the use of an acid hide powder.

Analysis of Sulphited Extracts.—The following method (Lepetit, *Collegium*, 1903, 234) may be employed:—

Estimation of Combined and Uncombined Sulphur Dioxide.—A round-bottomed flask of about 250 c.c. capacity is fitted with a three-holed rubber

bung. Through one of the holes passes a narrow glass tube reaching nearly to the bottom of the flask and connected with an apparatus for the automatic delivery of carbon dioxide. Through the second passes a funnel tube with glass tap, and through the third a delivery tube connected with a Peligotschen tube or other similar mechanism.

In the case of extracts containing less than 25 per cent. of bisulphite 10 grms. of the substance are taken, and for extracts containing more than 25 per cent., 5 grms. This is washed into the flask with about 125 c.c. of water, and the flask is connected with the absorption tube, which contains about 5 grms. of sodium bicarbonate dissolved in a little water.

Carbon dioxide is now passed in, the flask being at the same time heated, and 12 c.c. of dilute hydrochloric acid are added to the flask through the tap funnel. After heating for half an hour the flame is removed and the carbon dioxide passed through for about 10 minutes.

The contents of the Peligotschen tube are now carefully washed out, diluted with about 200 c.c. of water, and titrated with decinormal iodine solution.

For the determination of combined sulphurous acid the contents of the flask, after the expulsion of the sulphur dioxide, are dried on the water-bath, treated with soda and water, and carefully washed with the addition of a little saltpetre. The ash is dissolved in dilute hydrochloric acid, filtered and treated with barium chloride, and, after standing for 12 hours, filtered and weighed.

The combined sulphur dioxide can equally well be obtained by determining the total sulphur dioxide and deducting the volatile portion found above. For the determination of the total sulphur dioxide the extract is neutralised with carbonate of soda, evaporated to dryness, and washed with saltpetre as above.

Prepared quebracho extracts contain approximately the following:—

Water,	15.0
Soluble non-tannins,	9.0
Tannins,	78.0
Insoluble matter,	nil

Gambier.—This material is derived from the *Uncaria gambir* of the East Indies. The leaves of the shrub are gathered, boiled with water, and the extract filtered and allowed to set, after which it is cut into cubes. It contains much catechin. A good gambir should contain at least 60 per cent. of tannins. The solution of the extract for analysis is often very difficult to filter, and may require the addition of kaolin either when filtered through a 605 filter paper or a candle. In cases where it is necessary to filter more than once through a candle to obtain a perfectly clear filtrate, there is bound to be a small loss through evaporation, hence it is better to add some kaolin, which should be previously ignited and thoroughly washed.

Mangrove Bark.—This material is of comparatively recent introduction,

and opinions differ considerably as to its value. There are, according to Parker, about twenty distinct kinds of bark which all have different characteristic colours and tannin values, but a similar external appearance. The percentage of tannin seems to vary from 3 to 50. It is obvious, therefore, that the bark should never be bought except upon analysis. Drabble and Nierenstein (*Collegium*, 1907, 199) state that mangrove tannin gives a brownish precipitate with sulphuric acid, being unique in this respect. This reaction may be of use in detecting mangrove as an adulterant of quebracho. Extracts of the bark further give a green colour with ferric chloride, a precipitate with bromine water and formaldehyde and hydrochloric acid, the latter being red-brown in colour.

Chestnut (*Castanea vesca*).—This is generally used as an extract, and contains from 28 to 32 per cent. of tannin matters.

Oak.—Both bark and wood are used for tanning. The bark contains quercitannic acid and gives anhydrides and ellagic acid. It contains about 12 per cent. of tannins.

The wood is generally used for making extracts which are said to be adulterated. The extract should contain from 26 to 28 per cent. of tannins, and give a tintometer reading of 4 to 5 red and 20 to 25 yellow, when, measured in a solution containing 0.5 per cent. of tanning matter in a 1-in. cell (Procter, *Principles of Leather Manufacture*, 256). The following tests may be used to ascertain the purity of an oak wood extract:—The oak bark extract gives an immediate precipitate with bromine water, while wood extract gives one only on standing. If a few drops of the non-tannin solution or an alcoholic extract from the total soluble matter be added to strong sulphuric acid in a test-tube, quebracho or other catechol tannins will be indicated by a bright red colour, while with genuine oak wood only a yellow or brown colour is produced.

CHAPTER XI.

MINERAL TANNAGES.

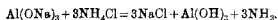
Alum and its Salts.—The chief points to be considered in the analysis of alum or aluminium sulphate or other salts are:—

- | | |
|----------------------------|-----------------|
| (1) Percentage of alumina. | (3) Total acid. |
| (2) Percentage of iron. | (4) Free acid. |

Determination of Alumina.—A weighed quantity of the salt is dissolved in water and made alkaline with ammonia. It is then heated on the water-bath for some time to expel excess of ammonia, since hydrated alumina dissolves in excess of ammonia with the formation of basic salts. The precipitate is then filtered off, washed with hot water till free from ammonia, dried and weighed as oxide of alumina, Al_2O_3 .

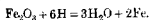
Determination of Iron.—If only present in traces the iron is determined volumetrically and allowed for in the precipitate as obtained above. If it be present in considerable quantities one of the following methods must be used:—

(a) The precipitate of alumina and iron oxide is fused in a platinum crucible with three or four times its volume of fusion mixture. It is then extracted with water and filtered, when the iron oxide will remain on the filter paper, the filtrate containing the alumina as sodium aluminate. The residual ferric oxide is ignited and weighed, and its weight deducted from the weight of the combined oxides. The alumina may be precipitated in the filtrate by the addition of ammonium chloride, which decomposes the aluminate as shown in the equation—



(b) A weighed portion of the mixed precipitate of iron and aluminium oxide is weighed into a porcelain boat; it is then placed in a combustion tube and ignited in a stream of hydrogen gas.

Ferric oxide is reduced by hydrogen to metallic iron; the alumina is unchanged. After the reduction is complete, re-weigh the boat, and from the loss of weight calculate the percentage of ferric oxide; a loss of 48 parts of oxygen corresponds to 160 parts of ferric oxide. This will be seen from the following equation:—



(c) The precipitate is digested for some time with sulphuric acid, and afterwards diluted, filtered, and thoroughly washed, the filtrate being made up to a definite volume. A measured quantity of this solution is now placed in a flask fitted with a cork, through which is passed a glass tube which is drawn out to a point, the end being broken off so as to form a small orifice through which hydrogen can escape. A weighed quantity of zinc is now placed in the flask together with a drop of platinum chloride solution, and the contents of the flask slightly warmed. The zinc will dissolve with the evolution of nascent hydrogen, which will reduce the ferric sulphate to the ferrous condition. When the zinc is dissolved and the solution is quite colourless a decinormal solution of potassium permanganate (made by dissolving 3.16 grms. in a litre of distilled water), is run in from a pipette, until a faint pink colour is produced. At this point all the ferrous sulphate will be oxidised to the ferric condition, and each c.c. of potassium permanganate used will correspond to 0.056 gm. of iron or 0.008 gm. of ferric oxide. If the zinc used be not free from iron, a blank experiment must be made with it and the necessary allowance made. The potassium permanganate solution should be standardised by the method already described under standard solutions.

Determination of Total Sulphuric Acid.—A weighed quantity of the salt is dissolved in water, acidified with hydrochloric acid, and boiled. While boiling, hot barium chloride solution is added slowly, and the liquid boiled for some minutes, after which it is allowed to settle and a little more barium chloride poured gently down the side of the beaker. If no further precipitate is formed, the barium sulphate is filtered off, washed with water, ignited, and weighed.

Hydrochloric acid may be estimated by titration with silver nitrate as described under water analysis.

Determination of Free Acid.—If free acid be present the aqueous solution will be acid to methyl orange and may be carefully titrated.

A better method is to precipitate the solution by means of absolute alcohol, in which reagent the free acids are readily soluble, while the neutral salts are not.

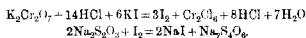
For this purpose the solution is concentrated to a small bulk and poured into a considerable excess of alcohol. After standing for some time it is filtered and the filtrate concentrated and the precipitation with alcohol repeated in order to throw down any neutral sulphates which had escaped the first treatment. After again filtering, the filtrate is considerably diluted and the free acid titrated with decinormal alkali and methyl orange.

Analysis of Chromates and Chromium Salts.—Chromic acid may be estimated either volumetrically or gravimetrically.

Gravimetric Process.—The solution is acidified with sulphuric acid, and diluted with a frequent addition of a little alcohol, until the whole

of the chromate is reduced to a chromium salt. Sulphur dioxide may also be used for the reduction, being either led in as a gas, or the acidified solution may be boiled with potassium metabisulphite. After the reduction is complete, the chromium is precipitated as chromium oxide, Cr_2O_3 , by means of ammonia. The mixture is then boiled till, on allowing the precipitate to stand, the supernatant liquid is quite colourless, after which it is filtered off, ignited, and weighed. The boiling is very necessary, since chromic oxide is distinctly soluble in alkaline solutions. If iron or aluminium salts be present, they may be precipitated with ammonia and filtered off before the reduction is carried out.

Volumetric Estimation.—This depends upon the fact that chromic acid is able to liberate iodine from potassium iodide, the liberated iodine being titrated with decinormal thiosulphate solution. A known volume of the solution to be analysed is placed in a stoppered bottle with about 5 c.c. of strong hydrochloric acid and an excess of potassium iodide added, the mixture being well shaken and allowed to stand for a short time. The decinormal solution of sodium thiosulphate is then carefully run into the bottle with shaking until the brown colour has nearly disappeared, when a little starch solution is added and the addition of the thiosulphate continued until the blue colour is just discharged. Each c.c. of decinormal thiosulphate used corresponds to 0.0049 gm. of potassium bichromate or 0.00173 gm. of chromium, as may be deduced from the following equations:—



Determination of Total Chromic Acid and Free Chromic Acid.—If bichromate and neutral chromate are present in the same solution, the bichromate may be determined by adding decinormal soda till the solution is just alkaline to phenolphthalein. Each c.c. used will be equivalent to 0.0147 gm. of potassium bichromate and 0.010 gm. of "half bound" or 0.005 gm. of free chromic acid (Procter, *L.I.L.B.*, 143). The above depends upon the fact that neutral chromate is neutral to phenolphthalein, while bichromate and free chromic acid are acid to it. From the above it will be seen that free chromic acid will require twice as much soda as when present as bichromate. The following rule is given by Procter:—"If the decinormal soda required to neutralise is less than one-third of the decinormal thiosulphate required for the chromium, each c.c. used corresponds to 0.010 gm. of chromic acid as bichromate or 0.0147 gm. of potassium bichromate, and the remainder of the chromic acid indicated by the thiosulphate will be present as neutral chromate. If the soda is more than one-third of the thiosulphate, each c.c. in excess of one-third will correspond to 0.010 gm. of free chromic acid, and the remainder indicated by the thiosulphate is bichromate. If the soda exceeds two-thirds of the thiosulphate the whole of the chromic acid is free, and the excess of soda is due to some other acid."

The following method of estimating free chromic acid is due to Messrs Procter and Heal (*J.S.C.I.*, 1895, p. 248), and depends upon the fact that hydrogen peroxide is able to oxidise chromic acid to perchromic acid, and that pure chromic acid dissolves in ether, forming a blue solution. A measured volume of the solution is placed in a small separating funnel, and 2 c.c. of hydrogen peroxide and about 20 c.c. of ether are added. The peroxide solution must be neutralised before use. Sufficient decinormal carbonate of soda solution is added to render the solution slightly alkaline, and it is then titrated with decinormal hydrochloric acid, shaking well after each addition until the ether acquires a faint blue tinge, which is best seen against a white background. If the volume of acid required to produce the blue colour is deducted from the volume of soda solution used, the difference is the soda used in converting the free chromic acid into bichromate, and each c.c. will correspond to 0.010 grm. of chromic acid (CrO_3).

A simple and rapid method is given by Dreher (*Collegium*, 1903, 111). One c.c. of the chrome solution is placed in a test-tube and 5 c.c. of a 10 per cent. sulphuric acid solution are added, then 10 c.c. of ether, and, finally, 5 c.c. of hydrogen peroxide solution. The mixture is now shaken and allowed to stand. The ether layer shows a blue coloration, and if 1 c.c. of several known chrome solutions of different strengths be treated in the same way (for example, solutions of 10, 20, and 40 grms. per litre), one can readily see which concentration corresponds to that of the solution under examination.

Determination of Chromium in Solutions of Chromium Salts.—In the absence of iron and alumina, chromium may be directly precipitated as described above, filtered off and weighed. Since, however, many of the solutions used contain notable quantities of alumina, it is best to convert the chromic oxide into bichromate and titrate. This is carried out in the following way. A measured volume of the solution, such as would correspond to about .5 grm. of total solids, is neutralised and treated with about 5 grms. of sodium peroxide, which is added in small successive quantities with continual stirring. After standing for a short time, the solution is boiled for about half an hour, adding water, if necessary, in order to completely decompose the excess of sodium peroxide. After boiling, the solution is acidified with hydrochloric acid, potassium iodide added, and the liberated iodine titrated as above with thiosulphate. The bichromate may also be determined by adding a standard solution of ammonium ferrous sulphate until a drop of the liquid, when placed in contact with a drop of potassium ferricyanide solution upon a white plate, gives a blue colour, showing that excess of ferrous salt is present. Excess of ferrous salt is added and the unused portion determined by adding decinormal potassium bichromate until a drop of the liquid no longer gives a blue colour with ferricyanide. From the total ferrous ammonium sulphate added deduct the excess calculated from the bi-

chromate solution used, when the difference will be ferrous salt oxidised by the original bichromate.

Procter and McCandlish (*J.S.C.I.*, 1907, 459) recommend this method as being very satisfactory. They find that it may be used in the presence of such bodies as gelatine, peptone, and glucose, and is therefore adapted to the analysis of used liquors. Titrating the liberated iodine with decinormal thiosulphate solution, each c.c. is equivalent to 0.0049 grm. of potassium bichromate or 0.00173 of chromium.

Estimation of Acidity in Chrome Liquors (Kopecky, *Collegium*, No. 247, p. 83).—A quantitative estimation of the chromium is first carried out in the following manner:—

To an amount of diluted chrome liquor containing from 0.1 to 0.15 grm. Cr_2O_3 a few drops of concentrated acid is added, and boiled for a few minutes. Precipitate by the least possible excess of dilute ammonia, wash first with water and then with alcohol to facilitate drying, and weigh. The precipitate consists of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$, and the percentage is calculated in terms of Cr_2O_3 and, to distinguish it from the true percentage of Cr_2O_3 present, called Cr_2O_3 (apparent). The ignited residue is then oxidised as described above, and chromium is determined with $\frac{\text{N}}{10}$ thiosulphate $\left(1 \text{ c.c. } \frac{\text{N}}{10} \text{Na}_2\text{S}_2\text{O}_3 = 0.00251 \text{ grm. } \text{Cr}_2\text{O}_3\right)$, and the result is calculated to per cent. Cr_2O_3 (true).

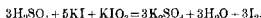
To determine the acidity, a quantity of liquor containing exactly 15.3 grms. Cr_2O_3 is weighed out and diluted to 1000 c.c. (It is not absolutely necessary to weigh out this quantity, but it simplifies calculations.)

To 50 c.c. of the solution, 2 grms. MgCO_3 are added and the mixture boiled till the carbonic acid is expelled. It is then cooled and made up to 100 c.c. and filtered. Fifty c.c. of the filtrate are pipetted into a beaker, and MgO estimated by the oxalate method. The weight of the residue multiplied by 4 gives the amount of MgO neutralised by the acid per 100 c.c. of the chrome liquor, or per 10 grms. of chrome alum, or per 1.53 grms. of Cr_2O_3 .

The results are returned as centigrammes of MgO which correspond to 10 grms. chrome alum or 1.53 grms. Cr_2O_3 .

Kopecky prefers the ammonium oxalate to the phosphate method for precipitating magnesia, since it is quicker. It is conducted as follows:—To the 50 c.c. of the filtrate used in the analysis, 3 or 4 grms. of crystalline ammonium oxalate are added with the application of heat and stirring. The solution is gradually raised to the boiling point, and 50 c.c. of acetic acid (80 to 90 per cent.) are added, with constant stirring, after which the mixture is kept boiling for a couple of minutes. After standing for six hours to complete precipitation the precipitate is filtered off and washed with a mixture of equal volumes of alcohol, water, and acetic acid. It is then dried and ignited in a covered crucible, and finally heated strongly to convert magnesium carbonate into magnesia.

Single-bath Chrome Liquors.—E. Steasing (*Der Gerber*, 1907, 33, 77-78, 91-92), recommends the following method for the estimation of acid of one-bath liquors, based on the action of acids on an iodide-iodate mixture according to the equation—

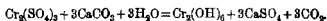


The process is as follows :—

To 10 c.c. of a fresh solution of potassium iodide (10 per cent.), 0.5 gm. of potassium iodate is added in solution, and 10 c.c. of the chrome liquor are introduced. A known quantity of sodium thiosulphate solution (30 c.c.) is added, the solution diluted to 150 c.c., and boiled for 5 minutes. It is then made up to 250 c.c., filtered, and to 150 c.c., 10 c.c. of $\frac{N}{10}$ iodine solution are added and the excess, titrated with sodium thiosulphate solution. Then, from the formula, $\{30 - \frac{x}{2}(10 - x)\}0.0048$, the quantity of acid is obtained, calculated as grms. "SO₄" in 10 c.c. of the chrome liquor.

Procter and McCandlish (*loc. cit.*) estimate acidity by titrating with sodium hydrate, using phenolphthalein as indicator, in a boiling solution. The process is accurate and rapid and is not vitiated by gelatin or peptones. In the presence of the latter bodies there is some tendency to frothing, which can be controlled by the addition of a few drops of turpentine. The chrome solution is diluted and boiled in a porcelain basin, 4 c.c. of a 1 per cent. solution of phenolphthalein being added. When the red colour of the phenolphthalein begins to disappear slowly, the burner is removed for the completion of the titration. Excess of alkali can readily be seen at the edge of the liquid against the side of the basin. This method is much shorter than Kopecky's, which requires a gravimetric estimation of magnesia.

Method of Appeltus and Schall for determining basicity of chrome liquors (*Collegium*, 1907, 266-268, 270-273). When chromium is precipitated with sodium hydrate or ammonia and filtered, the acids will be found in the filtrate in combination with the alkali, but if estimated in this filtrate the result will be too low, since the precipitated chromic oxide retains distinct quantities of alkaline salts. If the liquor be simply acidified with hydrochloric acid and precipitated with barium chloride for the determination of sulphuric acid, it is found that the barium sulphate is distinctly soluble in the acid chromic chloride solution, the error due to this cause being sometimes 2 per cent. If, however, a solution containing alkaline and chromic salts be treated with calcium carbonate, the acid combined with chromium liberates its equivalent of carbon dioxide, the alkaline salts being unaffected. The reaction proceeds in accordance with the equation—

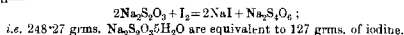


Five grms. of pure calcium carbonate are placed in a flask, which

is connected with a set of drying tubes and a soda-lime tube for the estimation of carbon dioxide. The flask is also provided with a tap funnel and an inlet tube, by means of which a current of air can be passed through the contained liquid. About 2 grms. of pure calcium carbonate and 40 c.c. of distilled water are now placed in the flask and boiled for about 10 minutes, a stream of carbon dioxide-free air being at the same time drawn through, the soda-lime tube being removed. While this is proceeding 50 c.c. of the chrome liquor (containing from 0.35 to 0.5 gm. Cr_2O_3) are boiled to expel carbon dioxide. The soda-lime tube is weighed and connected up and the boiled chrome liquor gradually introduced into the flask through the tap funnel, the boiling and passage of air being continued. After the whole of the liquor has been let in, the air is passed through for some minutes to expel the last traces of carbon dioxide. The experiment should take about 45 minutes. The soda-lime tube is now reweighed, the increase in weight being due to carbon dioxide. Three molecules of carbon dioxide are equivalent to three of sulphuric acid (SO_3).

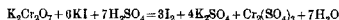
Procter and McCandlish, who have also examined this method, attempted to absorb the carbon dioxide in excess of standard sodium hydrate solution, and afterwards determine the excess of alkali and the sodium carbonate formed during the experiment by titration with standard acid, but the results were not so reliable as when the carbon dioxide is weighed.

Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, may be estimated by direct titration with decinormal iodine solution. Twenty c.c. of the iodine solution are placed in a flask, and the thiosulphate solution run in till the brown colour has faded to light yellow. A few drops of starch solution are then added, and the titration continued till the blue colour has just disappeared. The strength of the thiosulphate can be calculated from the equation—



A better method is the following :—

About 25 grms. of the thiosulphate are weighed and dissolved in 100 c.c. of distilled water. A measured quantity of standard potassium bichromate (30 c.c.) is mixed with 15 c.c. of a solution of potassium iodide made by dissolving 150 grms. of KI in 1 litre of water and 5 c.c. of hydrochloric acid. The iodine which is liberated in accordance with the equation—



is titrated with the thiosulphate solution, and the value calculated from the iodine found.

Dr Louis E. Levi (*J. American Leather Chemists' Association*, 1907, 127) quotes the following method for the analysis of sodium hyposulphite, which estimates not only sodium thiosulphate, but any sulphite, bisulphite, or sulphate which the sample may contain. A solution of 12 grms. to the

litre is titrated with $\frac{N}{10}$ HCl, using methyl orange as an indicator. One c.c. $\frac{N}{10}$ HCl = 0.252 grm. of $\text{Na}_2\text{SO}_5 \cdot 7\text{H}_2\text{O}$. The neutral solution with added starch is titrated with $\frac{N}{10}$ iodine. After getting the end point, one drop of $\frac{N}{10}$ thiosulphate is added to destroy the blue colour, and the solution is neutralised with $\frac{N}{10}$ NaOH. Subtracting two-thirds of the soda reading from the iodine reading, the difference multiplied by 0.248 gives the $\text{Na}_2\text{S}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. One-third of the soda reading *minus* the HCl reading gives NaHSO_5 (factor 0.104). For sulphate, 10 grms. of Rochelle salt are added to 5 grms. of the sample dissolved in water, the mixture left to stand over night, filtered, and sulphate determined in the filtrate with BaCl_2 .

CHAPTER XII.

THE ANALYSIS OF SPENT LIQUORS AND TANS.

THE following determinations are usually made:—

Total dissolved matter.

Suspended matter.

Mineral matter.

Tannins.

Volatile and fixed acids.

Total organic matter, including nitrogen and soluble leather.

Total Dissolved Matter.—The liquor is filtered through a 605 filter paper, with the addition of a little kaolin (if necessary), and 50 c.c. of the filtrate are evaporated to dryness and weighed.

Suspended Matter.—After thoroughly shaking the liquor, 50 c.c. are withdrawn as quickly as possible and evaporated to dryness and weighed; the difference between the weight of this residue and that of the total dissolved matter will be due to suspended matter.

Mineral Matter.—The residue from the total solids *plus* suspended matter is ignited and then treated with a little ammonium carbonate solution, evaporated to dryness on the water-bath, and gently ignited and weighed. The difference between the total solids and mineral matter will, of course, be organic matter.

Tannins.—The filtered liquor is diluted or concentrated until it contains about 5 grms. per litre of tannin matter, and is then analysed either by the official shake method, or the Palmer modification, or the Löwenthal.

The latter is most suitable for weak liquors, but the Palmer method is extremely useful for stronger materials.

Acids. Procter's Method.—**Total Acid.**—Ten c.c. of the filtered liquor are titrated in a beaker with lime water until a slight precipitate is produced. This is repeated several times and the average taken. The acid is calculated to acetic, factor '003, but it is advisable to standardise the lime water with decinormal acid and phenolphthalein. If oxalic acid or sulphuric acid is present, neutral calcium acetate or chloride is added to the liquor, which is made up to twice its original volume and filtered, 20 c.c. being titrated

instead of 10. Half the carbonic acid is estimated by this method, but it can be previously removed by adding salt and shaking, the liquid being made up to a definite volume before titration.

Volatile Acids are determined by distilling the liquor nearly to dryness, adding more water and redistilling, and finally titrating the distillate with decinormal alkali and phenolphthalein calculated to acetic acid.

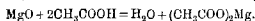
To determine the volatile acids present as salts, add phosphoric acid to the residue, dilute and re-distil and titrate.

Determination by Double Titration.—Determine the total acidity and then evaporate a measured volume to dryness on the water-bath. A little water is added and re-evaporated, after which the residue is dissolved, and the non volatile acid determined by titration. This deducted from the total gives the volatile acid. It should be noted that lactic acid is decomposed during distillation, and so not estimated by the direct distillation process. This objection does not apply to the double titration.

A.O.A.C. Method (J.S.C.I., 1907, 130). To Determine Total Acidity.—Dilute 100 c.c. of the liquor to 500 c.c. and place 100 c.c. of diluted liquor in a flask fitted with a reflux condenser; add 2 grms. of chemically pure animal charcoal and heat the mixture till it boils, with frequent shaking. Then cool, filter, and titrate with $\frac{N}{10}$ sodium hydrate and phenolphthalein.

A more accurate method is that of Kohnstein and Simand (Procter, *L.I.L.B.*, 127), which is carried out as follows:—

One hundred c.c. of the liquor are boiled with 3 to 4 grms. of freshly-ignited magnesia free from lime, and filtered. The magnesia is then estimated in the filtrate, any lime present being previously thrown down with ammonium oxalate. The magnesia in the filtrate is due to original free acid in the liquor, and is calculated to acetic acid by multiplying by 3.



Sulphuric acid may be estimated by evaporating a portion of the filtrate to dryness and strongly igniting. Magnesium sulphate will remain undecomposed, while the organic magnesium salts will form oxides insoluble in water. If this be filtered off and washed, the soluble magnesia may be determined and calculated to sulphuric acid. In this process the absence of magnesium salts in the liquors is assumed. If these are present, they must be estimated and allowed for. It is also important that the water used for washing should be boiled to expel carbonic acid, since magnesium carbonate will otherwise be formed, which is distinctly soluble.

The Estimation of Free Sulphuric Acid in Liquors.—The following method, due to Parker and Payne (*Collegium*, 1904, 96), is based on the insolubility of sulphates in 80 per cent. alcohol. Ten grms. of the liquor are placed in a 100 c.c. stoppered cylinder with 90 c.c. of absolute alcohol, and the mixture well shaken. The mixture is then filtered through a dry paper, which is washed with 90 per cent. alcohol. One c.c. of pure

hydrochloric acid is now added to the filtrate, and the sulphuric acid is then precipitated with 2 or 3 c.c. of a 10 per cent. solution of fine barium chloride. After warming on a water-bath, the precipitate is filtered off, washed, ignited, and weighed.

Procter's method for the determination of sulphuric acid in leather may be equally well applied to the analysis of tan liquors.

Acidity in tan liquors may also be determined in the following way, recommended by A. W. Hoppenstedt (*Collegium*, 1907, 77).

To 200 c.c. of a 10 per cent. solution of the liquor, 20 c.c. of quinine solution are added, mixed, and the whole filtered. One hundred c.c. of the filtrate are titrated with $\frac{N}{10}$ NaOH, using phenolphthalein as indicator. Multiply the c.c. used by 0.066 to obtain direct per cent. of acid (as acetic acid) in the original liquor.

The quinine solution is made by dissolving 15 grms. of pure quinine in 110 c.c. of neutral 95 per cent. alcohol, and then making up to 200 c.c. with water.

The quinine precipitates tannin and forms soluble salts with the free acid, which, however, are still acid to phenolphthalein, and can then be titrated as if in the free state.

Soluble Leather.—The detection and estimation of soluble leather in tan liquors may be effected by the method of Parker and Casaburi (*Collegium*, 1905, 210):—

Two hundred and fifty c.c. of the clear filtered liquor are neutralised with caustic soda in a 500 c.c. stoppered cylinder. Two hundred c.c. of a saturated solution of salt and 10 to 20 grms. of recrystallised salt are added, after which the mixture is well shaken and allowed to stand for several hours. Dissolved pelt or leather will be thrown out of solution and float on the surface, and may be approximately measured or weighed. For estimation of dissolved hide the following method is recommended. To 200 c.c. of unfiltered tan liquor is added 25 c.c. of a concentrated solution of acetate of soda, and ferric acetate is then added till no further precipitate is produced. The precipitate contains all the compounds of tannin, including soluble leather, ammonium salts remaining in solution. The precipitate is filtered off, washed, partly dried, and kjeldahled, the amount of hide-substance being calculated from the nitrogen content by multiplying by the fraction $\frac{100}{17.8}$.

Total Nitrogen may be determined by concentrating 25 c.c. previously acidified and kjeldahling; or the albuminoid nitrogen may be salted out with zinc or magnesium sulphates, filtered off and kjeldahled. The total nitrogen will include hide substance as well as ammonium salts, etc. It is obvious, however, that any nitrogen, by whatever method it is produced, is lost to the tanner.

Spent Chrome Liquors.—In the double-bath processes the spent

bichrome liquors need only be filtered and titrated with thiosulphate to determine the bichromate.

Single-bath Chrome Liquors require oxidation before they can be titrated. It is best to precipitate with ammonia, boil off the excess, and filter the precipitated chromic oxide. This is then washed into a beaker and treated with sodium peroxide, the mixture being subsequently acidified and boiled till all the hydrogen peroxide is expelled. It is then titrated with thiosulphate.

Analysis of Solid Materials.—Solid spent tanning materials are dried and finely ground and extracted in the same way as an ordinary tanning material. Since it is not possible to take sufficient for extraction to obtain an extract of the required strength, the solution must be boiled down until the necessary concentration is obtained. The boiling should be carried out either in the absence of air or in a flask in the neck of which a funnel is inserted, the ebullition being as rapid as possible. It is impossible to prevent a destruction of some tannin, and there is no doubt that Löwenthal's method is more suitable for these analyses than the hide-powder method. See the official I.A.L.T.C. method on p. 150.

CHAPTER XIII.

OILS.

THE number of oils that are occasionally used in a tan-yard is very large, but only a few are used in any quantity. In this chapter only the latter class will be dealt with. For fuller details or for information on other oils, Lewkowitsch's text-book of *Oils, Fats, and Waxes* should be consulted. The analysis of oils is, perhaps, one of the most difficult and important classes of work that a leather chemist is called upon to undertake. The difficulty arises from the complex nature of an oil, the purity of which can often only be inferred from a consideration of the data afforded by the determination of a number of constants, which will be hereafter described. The difficulty of the task of deciding absolutely in many cases renders sophistication comparatively easy. Hence the problem is one which should never be shirked. Fortunately a large number of data have been collected in the case of most of the oils used by tanners, and, while it is fairly easy to make an artificial oil that will pass one or two standards, it is not so easy to make one that will pass several. Hence, if an analysis be carried far enough, it is nearly always possible to detect adulteration. The following is a description of the chief methods used for the analysis of oils:—

Sampling Oils.—*Liquid Oils.*—Stir thoroughly or warm to incorporate any separated stearine or other insoluble matter, and remove sufficient for analysis before it again settles.

Solid Greases.—An auger is introduced into each cask and a cylindrical piece of the grease removed about 8 in. long and 1 in. in diameter. The net weight of the grease in each cask is also taken. After sampling each cask, or a sufficient number to obtain an average, the cylindrical portions removed are mixed in proportions corresponding to the net weights. After this the whole is melted on the water-bath and thoroughly mixed.

Determination of Water.—Five grms. of the oil are weighed into a dish provided with a stirrer, and dried, with frequent stirring, at 105° to 110° C. until constant in weight. It is necessary to weigh frequently, since oxidation often occurs on prolonged heating.

In the case of readily oxidisable oils the sample is weighed in a flask fitted with a rubber bung, through which passes a tube ending beneath the surface of the oil, and a delivery tube connected with a vacuum pump. By means of the latter a current of coal gas, previously dried by passing it through a calcium chloride tube, is drawn through the flask.

Where the percentage of water is high, as in cod oils, the following methods give the best results:—About 5 grms. of the oil are weighed into a nickel or other dish containing a stirrer. The dish is placed on a sand-bath and heated with a bunsen flame, the contents being well stirred the whole time. After a short time, if much water be present, the oil will begin to boil, and gentle ebullition is maintained till the whole of the water is expelled. When ebullition ceases, the flame is at once withdrawn and the dish placed in a desiccator to cool.

Insoluble Matter.—A weighed quantity of the oil is dissolved in petroleum ether and filtered through a weighed filter. The latter is subsequently dried and weighed, the increase being insoluble matter. The nature of the insoluble residue should be determined. The total fat may be at the same time determined by collecting the filtrate in a weighed flask, evaporating off the petroleum, and weighing the residue.

Very often, however, it is difficult to obtain a clear filtrate, and in this case the total fat is determined, when necessary, by mixing a weighed quantity of the fat with some silver sand or ignited gypsum, drying in the oven, and extracting in a Soxhlet extractor.

Impurities Soluble in Water.—Oils sometimes contain acids and certain mineral constituents, which may be removed by shaking with hot water. After shaking, the mixture is placed on the water-bath till the oil has separated, when the lower layer is run off by means of a separating funnel and tested.

Determination of Ash.—In estimating the ash given by an oil only a small flame must be used until the substance is completely charred, or some loss may occur. The ash may be dissolved in hydrochloric acid and tested in the usual way.

Oils used in tanning and currying must be free from iron. Its presence may be discovered as follows:—A weighed portion of the oil is shaken in a graduated cylinder with dilute sulphuric acid to dissolve the iron. A little potassium ferrocyanide solution and some ether are now added and the cylinder again shaken to separate the oil. In the presence of iron the lower layer will be blue owing to the formation of Prussian blue, and the quantity of iron present can be determined by matching the colour with that produced in similar quantities of iron-free oil and ferrocyanide by a standard iron solution.

Specific Gravity.—This may be determined with fair accuracy by means of Mohr's hydrostatic balance (fig. 31). The instrument measures the specific gravity by means of the loss of weight of a plummet when suspended in the liquid from one arm of a balance, weights being added till

the loss of weight is exactly counterbalanced. The beam is divided into a number of equal divisions by means of small projections on which the weights are hung, these being such that the specific gravity of the liquid may be read off directly without any calculation. The plummet displaces exactly 10 grms. of water at 15.5° C., and the weights or riders are arranged for four decimal places, weighing 10, 1, $\frac{1}{10}$ and $\frac{1}{100}$ grms. To make an experiment the balance is levelled by means of the screws until the pointer is at zero on the scale. The plummet is then immersed in the liquid to be tested, which is placed in the cylinder and brought to a temperature of 15.5° C. Owing to the displacement of the liquid the equilibrium will be now destroyed, and if the liquid used be distilled water the balance may be restored by hanging the 1 gm. weight at the

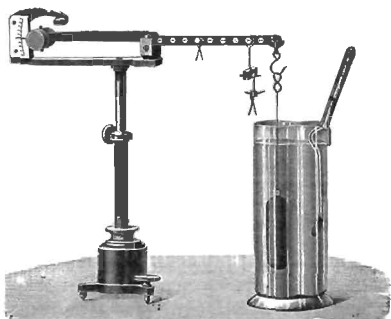


FIG. 31.

end of the beam. If the specific gravity of the liquid be different from that of water, either greater or smaller weights will be required. If it be, for example, 0.9, the balance will be restored by hanging the 1 gm. weight on the 9th projection from the centre. Having found between which two divisions the 1-gm. weight must be placed, and thus determined the first place of decimals, we take the $\frac{1}{10}$ -gm. weight and proceed in the same way to find the second place. In this manner all four places of decimals may be determined.

Determination by means of Specific Gravity Bottle.—The ordinary form of bottle may be used for sufficiently liquid oils, but the pycnometer form will in many cases be more useful. It is advisable in filling the bottle to introduce the oil through a pipette reaching to the bottom of the bottle. For great accuracy the *Sprengel Tube* should be used.

This consists of a V-tube, as shown in fig. 32, ending in two capillary tubes bent at right angles, and ground at their ends to fit glass caps. On

one of these tubes is a mark, and the internal diameter of this limb is about 0.5 mm., while that of the other limb should not be more than 0.25 mm. (Lewkowitsch, vol. i., p. 162). The tube is filled with the oil by sucking out the air from the narrower end, by attaching to an air-pump, or by sucking with the mouth through a piece of rubber connection tubing, the other end being immersed in oil.

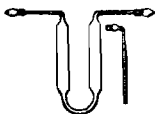


Fig. 32.

Many Sprengel tubes are supplied with a small tube which fits on the ground end and which has a small bulb near the joint. The fine end of the tube is sucked till the oil enters the bulb.

When the tube is full it is brought to the required temperature, and the volume of its contents adjusted till the oil just reaches the mark on the broader limb. Owing to the capillary force in the narrow tube the oil will expand and contract in the other tube only. If, after the desired temperature has been obtained, the oil reaches beyond the mark, a little is removed by means of a small piece of filter paper applied to the capillary end; while, if the oil is behind the mark, the end of the tube is touched with a glass rod dipped in the oil. When the volume has been adjusted the caps are put on and the tube weighed. This must always be carried out by suspending it from the hook of the balance by means of a platinum wire, which is conveniently weighed with the empty tube.

Having weighed the tube *plus* oil, this is removed, the tube cleaned with ether and dried, and its water-content determined in exactly the same way.

Temperature of Experiment.—In the case of many fats it is impossible to determine specific gravities at the standard temperature, since they are solid or semi-liquid at this point. In such cases their specific gravity at 100° C. compared with water at the standard temperature of 15.5° C. is generally taken. The hydrostatic balance may be used for this purpose.

The oil is placed in a wide test-tube which passes through a rubber bung fitted to a hole in a closed water-bath, the steam being led off by a tube which passes through a second rubber bung, so that no steam can condense on the balance. The water is boiled till the oil in the tube and the plummet have attained the same temperature, when the determination is made in the ordinary way.

Specific gravities at the boiling point may be very easily determined by means of the Sprengel tube. The tube is filled with the oil and placed in a beaker of water of such diameter that it remains suspended by the two limbs from the sides of the beaker. The water is now boiled until the oil has attained the temperature of the water and the volume then adjusted, the caps replaced and the tube and its contents weighed.

Melting Point.—The method of determining the solidifying point or titer will be described below. Melting points are very difficult to

obtain with anything like accuracy, and the results will vary somewhat according to the method used. For a description of the various methods, Lewkowitsch, vol. i., chap. v., may be consulted. The following process in the experience of the author gives good results:—A little of the fat is melted in a dish, and a loop of platinum wire small enough to hold some melted fat dipped in it. The fat removed by the loop is allowed to solidify and the wire suspended in a beaker of water in which a thermometer is immersed, together with a stirrer made of a circle of cork or glass, which can be vertically raised and lowered. The water is gently heated with

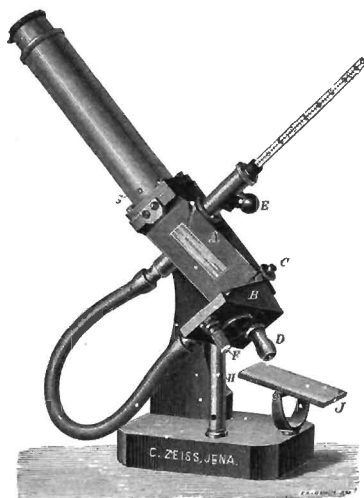


FIG. 33.

constant stirring until the fat melts, which is indicated by its becoming quite transparent or leaving the loop. The temperature at this point is the melting point of the fat.

Refractive Index.—The refractive index is very rapidly determined and is of much use in the examination of oils. In the case of cod oil, for example, the index lies between two fairly close limits, and a number outside these limits would indicate adulteration. The refractive index may be measured by means of the Abbe or Zeiss refractometers. The latter is most generally used. The apparatus is shown in fig. 33.

It consists of a telescope and two prisms, between which a drop of the oil is pressed into a film. Light is passed through the prisms by means of a reflector at the bottom, and the total refraction is observed through the telescope, the dispersion between the glass and film being compensated by that due to the surface of the double prism.

The experiment is performed as follows:—Connect the refractometer with the apparatus for supplying water at constant temperature. When the desired temperature has been reached, open the prism and rub over the surface a little of the melted fat or oil. The prism must, of course, be perfectly cleaned, this being best done with a little ether and a small piece of silk rag. The prisms are now closed and the mirror adjusted till the vertical line appears distinct when viewed through the telescope. If a satisfactory line cannot be observed, the surfaces of the prisms are probably not sufficiently covered with oil. After allowing sufficient time for the oil to attain a constant temperature, the position of the line is read and the refractive index determined by reference to Table XLVI.

TABLE XLVI.

Scale Division.	D.	Difference.
0	1.4220	
10	1.4300	8.0
20	1.4377	7.7
30	1.4452	7.5
40	1.4524	7.2
50	1.4593	6.9
60	1.4659	6.6
70	1.4723	6.4
80	1.4783	6.0
90	1.4840	5.7
100	1.4895	5.5

With each instrument a bottle of standard oil is supplied of a known index. The refractometer can be adjusted for this oil by altering the position of the objective with a watch-key. The critical line of this fluid is colourless, and occupies the following positions on the scale. The following table gives the constants of this oil:—

TABLE XLVII.

Temp.	Sc. div.	Temp.	Sc. div.	Temp.	Sc. div.	Temp.	Sc. div.
30°	68.1	25°	71.2	20°	74.3	15°	77.3
29°	68.7	24°	71.8	19°	74.9	14°	77.9
28°	69.3	23°	72.4	18°	75.5	13°	78.6
27°	70.0	22°	73.0	17°	76.1	12°	79.2
26°	70.6	21°	73.6	16°	76.7	11°	79.8
25°	71.2	20°	74.3	15°	77.3	10°	80.4

The fractional parts of a degree can accordingly easily be brought into calculation ($0.1 = 0.06$ scale div.). Deviations of 1 to 2 decimals of the scale divisions are of no consequence, and are in most cases due to inexact determinations of temperature. Should, however, careful tests result in the discovery of greater deviations, readjustment of the scale will be necessary, which may be effected by means of a watch-key supplied with the instrument, in accordance with the values given in the above table. The watch-key is inserted at *G* in fig. 33, and by its means the position of the objective, and, therefore, that of the critical line with respect to that of the scale, may be altered.

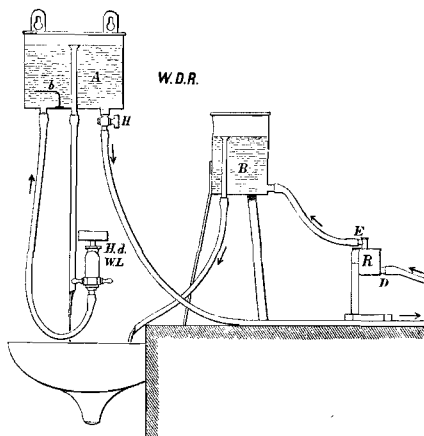


FIG. 34.

The constant temperature may be maintained by means of the apparatus supplied with the instrument, which is shown, fig. 34.

A is a cistern which is fastened to the wall about 3 feet above the level of the laboratory bench. It is supplied with water from the tap *H.d.*, the level being maintained constant by the vertical overflow. The water leaves the cistern at *H*, a tap being provided to regulate the flow. The tube from this tap is connected with a metal spiral enclosed in an air-bath and heated with a bunsen burner. The water after passing through the heated spiral enters the refractometer at *D*, leaving at *E* and passing into a second cistern *B*, also provided with an overflow to maintain a constant level. By means of a little adjustment of the rate of flow and the

height of the bunsen flame a constant temperature may be obtained in the refractometer.

The thermostat described by Thorpe (*J.C.S.*, 1904, lxxxv. 257-259, and *Analyst*, 1904, 135) is in some respects preferable. It consists of an apparatus for generating steam, containing a coil through which the current of water flows, and is heated before passing through the refractometer. A reflux condenser is provided to condense the steam. After passing through the spiral the water enters a cistern adapted to the maintenance of a constant head of water from which it enters the refractometer, afterwards passing to the waste pipe. The apparatus is capable of keeping a temperature within very narrow limits and is very quickly brought into action.

Unsapönifiable Matter.—About 5 grms. of the oil are weighed into a flask. Twenty-five c.c. of alcohol (rectified methylated spirit) and a small piece of stick potash (1-2 grms.) are added. The flask is then connected with a reflux condenser and the contents boiled with frequent rotatory agitation for about an hour. At the end of this time the flask is removed, an equal volume of distilled water added, and the whole poured into a separating funnel. The flask is washed with petroleum ether, this being also poured into the separating funnel. About 30 c.c. should be used. The contents of the funnel are now carefully rotated so as to bring the petroleum into contact with the soap solution without making an emulsion. Next allow the funnel to stand until the layers have separated, and then draw off the lower layer completely into the flask. The petroleum layer is now washed at least three times with distilled water to remove any dissolved soap. The first washing must be accomplished by rotation, but the third time the liquid may be well shaken. These washings are collected separately. The petroleum ether is finally poured into a weighed flask. The original soap solution is now returned to the separator and again extracted with ether. This time it may be shaken, as the tendency to emulsify will be less. The petroleum layer is separated and washed as before, and added to the weighed flask. The extraction is then repeated a third time, after which the total volume of petroleum ether is evaporated off and the residue weighed. If this seems excessive it should be redissolved in petroleum and washed again to remove any soap that may be present. If the previous washings have been carefully carried out this should not be necessary. It is sometimes desirable to re-saponify the residue, and re-extract. It must be carefully noted that soap is distinctly soluble in petrol, especially in the presence of alkali.

Alternative Method.—The original soap solution is poured upon a quantity of sand, the mixture dried, powdered, and extracted in a Soxhlet extractor with ether or petroleum. It is often advisable to substitute ordinary ether for petrol, or after extraction with petrol to extract with ether, thus dividing the unsapönifiable matter into two parts.

Saponifications and evaporations of residues may conveniently be

carried out by means of a simple electrical heater (Trotman and Hackford, *J.S.C.I.*, 1904, p. 1137), which prevents any danger of ignition of inflammable vapours.

The apparatus is a simple contrivance, consisting of a tin, some 6 in. or 8 in. deep, and of sufficient diameter to take a lamp of 16, 32, or 50 candle-power. The exterior is covered with asbestos paper. The lamp is of the ordinary type, but the greatest heat is obtained from lamps discoloured by continual usage, and which can be obtained at a trifling cost from dealers in electric light fittings. The lamp is fixed through a hole near the bottom of the tin, as shown in fig. 35. The holder, lamp, and tin are placed on a wooden base, the top surface of which is covered with asbestos beneath the tin.

The lamp is useful for saponifications, fat extractions, and the distilla-

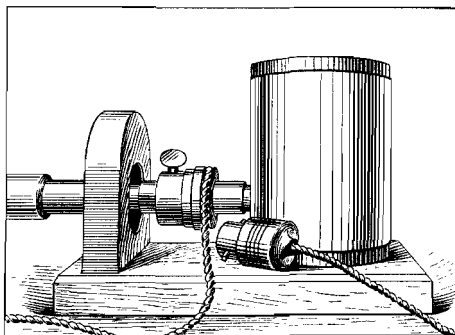


FIG. 35.

tion of alcohol and ether, the source of heat being perfectly constant and unaffected by draughts, and it is impossible for inflammable liquids to be ignited.

If methylated spirit be used for this and other determinations it should be rectified by the following method (*Analyst*, 1890, 50):—The spirit is treated with powdered potassium permanganate till a permanent pink colour is produced. After standing for some time a little calcium carbonate is added and the spirit distilled, using a Wurtz or Le Bel Henniger tube, the rate of distillation being maintained at 50 c.c. per 20 minutes. The distillate is frequently tested by boiling 10 c.c. with 1 c.c. of strong potash solution and allowing to stand for 30 minutes, and so long as any colour is produced it is rejected. Carter Bell recommends distilling in presence of a mixture of soap and potash.

Methylated spirit should, before use, always be tested for unsaponifiable matter.

Fatty Acids.—If these be required, the soap solution and washings obtained in the determination of unsaponifiable matter are freed from alcohol and petroleum on the water-bath. The soap is then dissolved in distilled water and transferred to a separating funnel, where it is acidified with hydrochloric acid and about 30 c.c. of ether added to dissolve the liberated fatty acids. The ethereal layer is washed as described above, after which it is transferred to a weighed flask, the ether evaporated off, and the residual fatty acids weighed.

Acid Value or Proportion of Free Fatty Acids.—Five grms. of the oil are warmed with neutral spirit and frequent shaking to dissolve out the free acid. Phenolphthalein is then added and decinormal soda until a faint pink colour is produced. The acid is then calculated as oleic acid, each c.c. of alkali being equivalent to 0.0282 gm.

Saponification Equivalent or the number of milligrammes of caustic potash required for the saponification of 1 gm. of fat. An approximately seminormal solution of alcoholic potash will be required. It is important that the alcohol used should develop no colour. The solution may be prepared by mixing the necessary volume of 50 per cent. aqueous solution made from potash purified by alcohol with rectified methylated spirit. After standing for some time the liquid is filtered into a rubber-stoppered bottle. The exact strength of this solution need not be known. The determination is performed as follows:—

One to two grms. of the oil are weighed into a flask of about 150 c.c. capacity, 25 c.c. of the alcoholic potash are run in from a pipette, and at the same time another 25 c.c. into a similar empty flask. Care should be taken that an exactly equal number of drops are allowed to drain from the pipette. The flasks are now covered with small watch-glasses placed on the water-bath, and occasionally agitated till the fat has saponified. Usually about 20 minutes will be required if the alcohol be kept gently boiling. At the end of this time the glass plates are rinsed back into the flasks with a little spirit to make good that lost during saponification. Phenolphthalein is then added to each flask and the unused potash titrated with seminormal hydrochloric acid. The number of c.c. required by the blank experiment will give the volume of seminormal potash added, while the acid used for the neutralisation of the unused potash in the saponification will measure the unused seminormal alkali. Hence the difference between the two readings will give the number of cubic centimetres of seminormal alkali required to completely saponify the weight of fat taken. This number multiplied by 0.028 gives caustic potash, from which can be calculated the number of milligrammes per one gramme or the saponification equivalent.

Iodine Value.—This means the percentage of iodine absorbed by an oil, and is a determination of the utmost importance in its examination,

being a measure of the unsaturated fatty acids present. The following solutions are required :—

Solution of Iodine (Wij's).—9.4 grms. of iodine trichloride and 7.2 grms. of iodine are dissolved in separate portions of glacial acetic acid in flasks which are covered to prevent absorption of moisture. When dissolved the two solutions are poured into a 1000 c.c. flask and made up to the mark with glacial acetic acid.

Lewkowitsch recommends the following method of preparation on account of cheapness :—Thirteen grms. of iodine are dissolved in a litre of glacial acetic acid and the exact amount of iodine present determined by titration with thiosulphate. Washed dry chlorine is now passed through the solution till the original titer is exactly doubled, *i.e.* until all the iodine is present as iodine mono-chloride, the solution at this point undergoing a distinct change in colour. The solution, having been made in either of the above ways, is titrated with decinormal thiosulphate and its iodine value determined. If carefully kept it will remain unchanged for a long time. If only used occasionally it should be titrated each time.

Decinormal Sodium Thiosulphate Solution (see p. 13).

Chloroform or Carbon Tetrachloride, which must absorb no iodine. It is tested by mixing 10 c.c. with 10 c.c. of iodine solution, and, after some time, titrating. The volume of thiosulphate required should be exactly the same as for 10 c.c. of the iodine solution.

Starch Solution.—Five grms. of soluble starch is made into a thin paste with water, and poured, with stirring, into 50 c.c. of boiling water. The solution must be freshly made each day.

Potassium Iodide Solution.—A 10 per cent. solution is used. The iodide must be free from iodate, since the latter, when treated with hydrochloric acid, gives free iodine.

Method of Performing Experiment.—From .3 to .5 gm. of the oil are weighed into a well-stoppered white-glass bottle of about 500 c.c. capacity and 10 c.c. of chloroform are added.

Lewkowitsch gives the following quantities as suitable :—

Drying or marine animal oils	0.15 to 0.18
Semi-drying oil,	0.2 0.3
Non-drying oil,	0.3 0.4
Solid oil,	0.8 1.0

Twenty-five c.c. of the iodine solution are then run in from a pipette, the stopper replaced, and the bottle allowed to stand in a dark place for an hour. Great care must be taken to always deliver the iodine solution in the same way. If a clear solution is not formed after the addition of the iodine solution, more chloroform is added. If during the experiment the colour becomes light brown, more iodine solution should be added, since the absorption only takes place regularly in the presence of excess of iodine. At the end of an hour 20 c.c. of the potassium iodide solution are added and decinormal thiosulphate solution run in from a burette until only a

faint brown colour is left. A few drops of starch solution are now added and the titration continued until the blue colour has just disappeared. The number of cubic centimetres of thiosulphate used deducted from the number required for 25 c.c. of the iodine solution gives the equivalent in thiosulphate of the iodine absorbed by the weight of oil taken for the experiment.

Hubl's Process.—Hubl found that from an alcoholic solution of iodine in the presence of mercuric chloride oils absorbed iodine in a regular, well-defined manner, and the method is preferred by some to the Wijs process.

The iodine solution so used is made by dissolving 25 grms. of pure iodine in 500 c.c. of 95 per cent. pure alcohol, and mixing with it 30 grms. of mercuric chloride ($HgCl_2$) dissolved in the same volume of pure spirit, the latter being filtered if necessary. The mixed solution changes rapidly

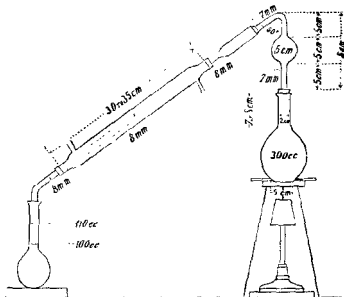


FIG. 36.

during the first hours after mixing, and should be allowed to stand 12 or 24 hours before using. It changes more slowly afterwards, and some chemists only mix so much of the two solutions as is required for one test. The details of a determination are the same as in Wijs' modification, except that the Hubl process requires a much longer time. Solid fats and non-drying oils must be left for 6 or 8 hours, drying oils and fish oils 12 to 18, to ensure complete absorption.

Volatile Fatty Acids.—Certain oils, such as butter fat, cocoanut oil, porpoise oil, dolphin oil, are distinguished from other oils by the large proportion of volatile fatty acids which they contain. The Reichert-Wolny process for their determination is only capable of limited application to tanyard oils, but may be described here. Five grms. of the filtered fat are weighed in a 300 c.c. flask (fig. 36) having a neck 7–8 cm. in length and 2 cm. in diameter. Two cubic centimetres of a solution of caustic soda (made by dissolving 100 grms. of pure caustic soda in 100 c.c. of water)

and 10 c.c. of pure alcohol are added, and the mixture heated under an inverted condenser for 15 to 20 minutes. The alcohol is then completely evaporated on the water-bath, after which the dry soap is dissolved in 100 c.c. of hot distilled water. When the soap is all dissolved, 40 c.c. of normal sulphuric acid and a fragment of pumice-stone are added, and the flask connected with a condenser by means of a connecting tube 15 cm. in height and 7 mm. in diameter, and with a bulb 5 cm. in diameter at a point 5 cm. above the cork. The flask is supported on a piece of asbestos having a circular hole of about 12 cm. diameter, and is heated with a small flame until the fatty acids are quite clear, after which 110 c.c. are distilled off in about 30 minutes. The distillate is well mixed and filtered through a dry ribbed filter, 100 c.c. being collected in a graduated flask. Phenolphthalein is added to this, and it is titrated with decinormal soda. The number of cubic centimetres required for neutralisation *plus* one-tenth is known as the Reichert-Wollny number. The following are a few of the fats having a high Reichert number:—

Dolphin oil,	5.6
Porpoise oil,	23.5
Cocoanut oil,	8.0
Butter fat,	27

The number for the bulk of the other oils is less than 1.

Oxidised Fatty Acids.—These acids, which are produced by the oxidation of oxidisable oils, are characterised by being insoluble in petroleum ether. Their determination is of considerable importance to the tanner. Five grms. of the oil are saponified, as in the estimation of unsaponifiable matter, and the alcohol evaporated off. The soap is then dissolved in water and the solution placed in a separating funnel and acidified with hydrochloric acid. Petroleum ether is then added, the funnel well shaken and allowed to stand. The unoxidised fatty acids and unsaponifiable matter will dissolve in the petroleum, but the oxidised will remain as a brown precipitate between the two layers, or sometimes adhering to the sides of the funnel. The lower layer is now drawn off and the petroleum ether poured out through a filter, care being taken to leave as much of the undissolved portion as possible in the filter funnel. The residue is washed several times with petroleum ether, after which it is dissolved in hot alcohol and filtered through the filter into a weighed flask or dish. The filter is washed once or twice with warm alcohol, and the solvent is evaporated and the residue weighed. If a dish be used, it should have vertical sides and never be more than half filled, since the solution of the acids has a great tendency to creep over the sides. This test may advantageously be applied to the soap solution after extraction of the unsaponifiable matter, the oxidised and unoxidised fatty acids being simultaneously determined.

Phytosteryl Acetate Test.—This test is of great importance in deciding whether an animal oil contains a vegetable product. The unsaponifiable

matter of animal oils contains cholesterol, while in that of vegetable oils phytosterol replaces it. Hence the detection of phytosterol in an animal oil points with certainty to the adulteration with an oil of vegetable origin. The test is performed as follows (Lewkowitsch, *Oils, Fats, and Waxes*, p. 372):—

The unsaponifiable matter is dissolved in ether and transferred to a small dish, and exposed to the air till the ether has evaporated. The residue is dried on the water-bath and heated in a dish with 2 to 3 c.c. of acetic anhydride for a minute over a small flame until it boils, the dish being covered with a watch-glass. The excess of acetic anhydride is then evaporated on the water-bath. The residue is dissolved with a small quantity of hot alcohol, and the solution allowed to spontaneously evaporate until crystallisation takes place. The crystals are filtered and washed with 95 per cent. alcohol, and then redissolved in alcohol and recrystallised as before. The melting-point of these crystals is determined. Cholesterol acetate melts at 114.3° to 114.8° C., while phytosterol acetate melts at 125° C. to 137° C. Hence the melting-point of this crop of crystals should show if phytosteryl acetate is present. It is generally, however, necessary to redissolve and recrystallise once or twice more. When the melting-point is no higher than 116° C. the absence of phytosteryl acetate is fairly certain.

Thermal Reaction with Sulphuric Acid: Moutoné Test.—This depends upon the fact that when oils are mixed with concentrated sulphuric acid a rise of temperature is produced depending on the nature of the oil. Drying oils give the greatest rise. The following modification of the original test is due to Archbutt (*J.S.C.I.*, 1886, 304). Exactly 50 grms. of the oil are weighed into a beaker of 200 c.c. capacity. The beaker and acid to be used in the experiment are placed in a bath at 20° C. until they have attained a constant temperature. The beaker is then removed and placed in a cardboard box having hollow sides, filled with cotton-wool. A thermometer is immersed in the oil, and, after the temperature has been noted, 10 c.c. of the sulphuric acid are added, the oil being continuously stirred with the thermometer, and the addition of the acid occupying exactly 1 minute. The highest point which the thermometer reaches is carefully noted.

The Bromide Value.—The difference in solubility of brominated glycerides and fatty acids according to the amount of bromine they contain has been used to gain further information as to the purity of oils. Hehner and Mitchell's "hexabromide test" was based upon this, but gave variable results. Procter and Bennett (*J.S.C.I.*, 1906, 798) have improved the method and obtained concordant results with a number of marine oils. Their method is as follows:—

About 4 gm. of the oil is weighed out into a small tared flask, 10 c.c. of carbon tetrachloride and 12 drops of bromine are added slowly through a tap funnel, and the mixture cooled for 3 hours in running water. Excess

of bromine is removed by adding .075 grm. of phenol dissolved in 10 c.c. of carbon tetrachloride, followed by the gradual addition with constant stirring of 20 c.c. of absolute alcohol. The mixture is filtered and allowed to drain, the precipitate washed with 50 c.c. of absolute alcohol, placed in a weighing bottle previously tared along with the filter paper, heated for 15 minutes in a steam oven, cooled in a desiccator, and weighed.

$$\frac{\text{Weight of bromide}}{\text{Weight of oil}} \times 100 = \text{bromide value.}$$

The amount of bromine in the precipitate may be determined, and the total bromine absorbed by the oil being calculated from its iodine value, the difference will give the percentage of bromine absorbed which is combined with the glycerides in the precipitate.

Example.—0.4138 grm. of cod oil gave 0.2502 grm. of precipitate, containing 0.1591 grm. of bromine. From the bromine value it is found that 0.4138 grm. of cod oil absorbs 0.3927 grm. of bromine. Hence the percentage of total bromine absorbed, which is taken up by the glycerides giving precipitates

$$= \frac{0.1591 \times 100}{0.3927} = 40.5.$$

The following list of bromide values is given by the authors:—

Brown cod,	60.4	Menhaden oil,	52-54
Newfoundland cod,	60.0	Seal,	13-15
Moller's cod,	40.6	Whale,	27-37
Linseed,	25.0		

Hexabromide Test of Hehner and Mitchell (*Analyst*, 1898, 313). This test is carried out as follows:—About 2 grms. of the oil are dissolved in 40 c.c. of ether containing a few drops of glacial acetic acid. The solution is cooled to about 5° C. in a corked flask, and bromine is added slowly till a permanent brown colour is produced. After 3 hours the precipitated hexabromides are filtered through an asbestos plug and washed with cooled glacial acetic acid, alcohol and ether, 5 c.c. of each being used. The precipitate is then dried in the water oven and weighed. Lewkowsitch (*Oils, Fats, and Waxes*, p. 314) gives the following values:—

Linseed oil,	23-37	Shark oil,	22
Cotton seed oil, }	nil	Seal oil,	27-54
Olive oil, }		Whale oil,	15-25
Fish oil,	49-52	Sperm oil,	2-3.69
Cod oil,	30-42		

Cod Oil.—Cod liver oil is prepared from the livers of the cod-fish, chiefly in Norway, Newfoundland, and Scotland. The Newfoundland oil is the best variety. A fourth variety, known as "coast cod," is manufactured in England from miscellaneous fish livers. The crude cod oil used by tanners is chiefly obtained from livers that have undergone a certain amount of putrefaction, and to this they owe their characteristic colour and

smell. Turnbull (*Collegium*, 1905, 177) gives the following constants for genuine cod oils:—

Specific gravity,	·9279-	·9342
Refractive index,	1·4815-	1·4834
Saponification value,	186·1	~189·5
Iodine value,	162·6	~172·7
Acid value,	8	~ 20
Specific temperature reaction,	253·8	

The chief adulterants are shark, menhaden, rosin, fish oils and mineral oils.

Rosin and mineral oils will readily be detected by the large amount of unsaponifiable matter they contain. If rosin oil be suspected, some of the oil should be saponified and the fatty acids liberated, collected, and dried. About 1 *gram*. of the acids is then warmed with acetic anhydride, and, after cooling, the clear portion drawn off with a pipette and treated with one drop of strong sulphuric acid. If rosin be present, a fugitive violet colour will be produced.

Shark oil contains a considerable quantity of unsaponifiable matter (10 per cent. ; while cod liver oil contains as a rule less than 0·5 per cent.). In badly-prepared oils the unsaponifiable matter may rise to 1 or 1·5, but rarely higher. The author has, however, examined cod oil giving the following figures, and which has worked perfectly satisfactorily:—

Iodine value,	155
Free acid,	9·0
Unsaponifiable matter,	4·5

Menhaden oil is indicated by a low iodine value. A genuine cod oil is never lower than 165, while that of menhaden oil is about 159. The specific temperature reaction is also of value in detecting menhaden. Turnbull gives the following figures:—

Cod liver oil,	252·8
Menhaden oil,	292·3

All the adulterants of cod liver oil, with the exception of linseed, would lower the iodine value. Linseed oil (iodine value 177) is very difficult to detect. If suspected, the phytosteryl acetate test should be performed. The acid value of a good cod oil should not be above 20 nor less than 10. A much higher value will indicate rancidity and liability to cause "spueing."

Determination of Resin in Cod Oil.—If the presence of resin acids be suspected, a quantity of the fat is saponified and the fatty acids liberated, washed, collected, and dried. About 3 grms. of the acid are weighed and heated with hydrochloric acid (as described for soap). The ethereal solution containing the esters of the fatty acids and the free resin acids may be examined either gravimetrically or volumetrically. The former is more accurate, but the volumetric method is much quicker, and sufficiently

accurate for most purposes. After the ethereal layer has been thoroughly washed, the water is run off and some alcohol added, and the resin acids titrated with decinormal sodium hydrate and phenolphthalein. Each cubic centimetre of decinormal alkali used will neutralise 0.346 gm. of resin acid. If the gravimetric process be adopted, the ethereal layer is washed with dilute alkali, which dissolves the free resin acids. The solution of resin soap is run into a second separating funnel and acidified in the presence of ether. The ethereal solution of the resin acids is separated, the solvent driven off, and the residue weighed.

•**Shark Oil** is never knowingly employed in English tanning, but is sometimes used to adulterate cod liver oil. Its high percentage of unsaponifiable matter, sometimes reaching 10 per cent., is accompanied by a low iodine value (90-136) and a specific gravity lower than that of cod oil. Hence, if a sample of cod oil has a low iodine value and specific gravity, and gives more than 10 per cent. of unsaponifiable matter, shark oil is probably present. The following samples of genuine shark oils obtained by the author show that there is some doubt as to these figures :—

TABLE XLVIII.

Shark Oil.	Unsaponifiable Matter.	Iodine Value.	Saponification Value.	Acid Value.
Crude,	0.62	104.1	...	7.7
Clarified,	8.07	143.5	167.5	3.5

Seal Oil.—There are four classes of seal oil, viz., water white, straw seal, yellow, and brown, the colour depending upon the length of time that the oil has been left in contact with the body before extraction (Lewkowitsch, p. 673). The brown variety is naturally rancid, and contains a larger percentage of free fatty acids than the others.

The limit of unsaponifiable matter is 0.5 per cent.

Seal oil is chiefly adulterated with fish oils, which are frequently betrayed by taste and smell. Mineral and rosin oils are sometimes used, but their detection is easy, since seal oil contains so little unsaponifiable matter.

Whale Oil.—There are a great many different kinds of whale oil, all of which have slightly different characteristics. A table of these will be found in Lewkowitsch, p. 675. The amount of unsaponifiable matter is somewhat variable, but never exceeds 3 per cent. The iodine value varies from 110 to 136. The saponification value is about 188. Rosin oil is said to be the chief adulterant. The titer of the fatty acids, 22°-23° C., is an important test of purity.

Fish Oil.—As showing the difficulty of deciding upon the purity of

cod oil, the following are the figures for three fish oils admittedly not cod oils:—

TABLE XLIX.

	1.	2.	3.	Cod Oil.
Unsaponifiable,	3.3	3.91	1.45	6-1.5
Iodine Value,	170	164.5	163.0	153-171
Saponification Value,	176.2	176.1	186.2	170-190
Refractive Index,	1.4759	1.4753	1.4741	1.4760-1.4800
Specific Gravity,9278	.9294	.9268	.9220-.9410

Neatsfoot Oil is made from the feet of cattle and other animals by boiling in water and skimming off the fat. It is considerably adulterated with vegetable oils, chiefly cotton-seed and rape, whose presence is indicated by a high iodine value, that for neatsfoot oil being 66-76. Vegetable oils may be detected with certainty by the phytosteryl acetate test. A special test for cotton-seed oil is the following:—One to three c.c. of the oil is dissolved in an equal volume of amyl alcohol. To this is added 1 to 3 c.c. of carbon bisulphide holding in solution 1 per cent. of flowers of sulphur. The mixture is heated in hot water until the carbon bisulphide has evaporated, when, if cotton-seed oil be present, a deep-red coloration will be produced in from 10 to 15 minutes (Lewkowitzsch). By this test 5 per cent. of cotton-seed oil may be detected, providing it has not been heated.

Olive Oil.—Genuine olive oil should have a specific gravity of 0.914 to 0.920. The free acid calculated as oleic should not exceed 5 per cent., and the unsaponifiable matter is never above 1 per cent. The iodine value ranges from 81.6 to 85, and the saponification value from 185 to 196. The chief adulterants are arachis oil, sesamé oil, cotton-seed oil, arachis or earth-nut oil, and rape oil. These will generally be indicated by the determination of the usual constants. Five per cent. of earth-nut oil may be detected by Bellier's test (*J.S.C.I.*, 1899, 303). One c.c. of the oil is saponified with 5 c.c. of 8.5 per cent. alcoholic potash, the mixture being kept boiling for 2 minutes, and then neutralised with acetic acid, mixed thoroughly, and rapidly cooled in water at 17°-19° C. When no more precipitate is formed, 50 c.c. of 70 per cent. alcohol containing 1 per cent. by volume of hydrochloric acid are added, and the mixture well shaken and replaced in the water. If more than 5 per cent. of earth-nut oil were present a distinct precipitate of arachidic acid is formed. Sesamé oil may be detected by Bandonin's test. 0.1 gm. of sugar is dissolved in 10 c.c. of hydrochloric acid of 1.19 specific gravity, and 20 c.c. of the oil are added, the mixture being thoroughly shaken. After standing for a minute to allow the aqueous solution to separate, the latter will, in presence of sesamé oil, be coloured crimson. Cotton-seed oil can be found by the Halphen test already described.

Castor Oil.—The specific gravity of castor oil should never be below 0.960. The following are its chief analytical constants:—

Iodine value,	85-86
Refractive index,	1.4799
Saponification value,	183-186

Turkey-red Oil.—If prepared from pure castor oil no precipitate should be produced when an aqueous solution of the oil is made alkaline with ammonia, even after standing for some hours. A turbidity or precipitate indicates adulteration. If the sample is boiled with dilute sulphuric acid and the oily layer separated, the latter should dissolve in four volumes of *rectified spirit* at 15° C., castor oil being more soluble in spirit than any oil likely to be used for its adulteration. The total fatty matter may be determined by acidifying and extracting with ether. The proportion of fatty acids present is usually about 50 per cent.

Tallow is the collective fat from the whole carcase of certain mammals, chiefly sheep and oxen. It is mainly a mixture of the triglycerides of palmitic, stearic, and oleic acids. Mutton tallow melts at about 45° C.; beef tallow, containing less stearin, is softer, and melts at about 40° C. Both should be nearly white and odourless. Adulteration with inferior fats, such as goat tallow and distilled grease stearin, imparts to the tallow their peculiar smell. Cotton-seed or other vegetable oil may be detected by the phytosteryl acetate test. When pure, tallow melts to a clear liquid, much turbidity indicating water or foreign mineral matter. Traces of bone and tissue may be accidental, but lime or lime soap is sometimes added to make the tallow hold more water. An analysis of tallow should include the determination of unsaponifiable matter, free acid, and total fatty acids. Saponification value and the titer and iodine value of the fatty acids may also be determined, more than 4 per cent. of free acid showing undue rancidity.

	Beef Tallow.	Mutton Tallow.
Iodine value,	34-45	32-46
“ “ of fatty acids,	25.41	35
Saponification value,	193-200	192-195

Linseed Oil is used in the preparation of “Japan” for patent leather and to some extent in currying. The raw oil may be adulterated with other seed oils and mineral oil, when the high specific gravity (.932-.936) of the pure oil will be lowered. To adjust a density so decreased rosin oil is sometimes added, but may be detected qualitatively by the Liebermann-Storch reaction, or quantitatively by warming with alcohol and titrating the alcoholic extract with phenolphthalein and normal potash, deducting from the volume used that required by the free fatty acid (up to 43 per cent.) always present in linseed oil.

The best test for the purity of linseed oil is its iodine value, higher than that of all common fatty oils. A value below 170 almost certainly

points to adulteration, though a higher one is not a certain proof of purity, a considerable proportion of fish and rosin oils not appreciably lowering it. Fish oil is difficult to detect chemically, but often the smell of the heated oil will betray it.

The hexabromide test is useful. Lewkowitsch states that pure linseed oil yields 38 per cent., and the fatty acids, which he brominates in preference to the oil itself, 30 to 42 per cent. of hexabromide (m.p. 175°-180°). Common adulterants yield little or none.

Extensive admixture with inferior oils must impair the superlative drying properties of linseed oil. In practised hands a comparison as to time of drying and resulting surface of the films of doubtful and standard samples spread on glass plates is a useful adjunct to chemical tests.

Waxes.—Of the waxes used by leather dressers beeswax is much subject to adulteration. Pure beeswax dissolves completely in chloroform; paraffin wax, carnauba wax, ceresin and wool wax (its common adulterants) do not; but the bleached wax is with difficulty soluble in chloroform, and thus incomplete solution of a pale sample is no proof of its impurity. Boiling with ether will wholly dissolve beeswax and any other waxes mixed with it, but serves to expose gross impurities, such as water, mineral matter, starch, and flour. Beeswax that has only been strained always contains pollen grains visible under the microscope. Specific gravity determinations are not of much value, since waxes may be mixed in such proportions as to produce a blend of the same density as pure beeswax. The most trustworthy test of purity is a determination of the acid value and saponification value. For the acid value 3 to 4 grms. of the wax should be heated with 20 c.c. of strong alcohol and titrated with seminormal alcoholic potash, using phenolphthalein as indicator, being careful to keep the wax in a melted state. The acid value of pure beeswax is about 18. Complete saponification is difficult. Seminormal potash made with absolute alcohol should be used and the mixture boiled for quite an hour. Some chemists use amyl alcohol to obtain a higher temperature, others ensure saponification by using sodium ethoxide. Pure beeswax has a saponification value of about 90.

Carnauba Wax, a hard wax melting at 105° C., is a frequent adulterant of beeswax, but is itself specially used for brown boot polish. As in the case of beeswax the acid and saponification value are the best tests of purity. Saponification is difficult, as with beeswax, and the values obtained for pure wax vary from 78 to 83. A high percentage of unsaponifiable matter indicates ceresin and paraffin. The acid value is about 4, a number much above this pointing to stearic acid.

Japan Wax forms an emulsion with water and is used for currying leather. It is not chemically a wax, as shown by its high saponification value—about 220. Its specific gravity is the same as that of water, with which it is often adulterated to the extent of 20 or 30 per cent. Adulteration with other fats is easily detected by the lowering of density.

Admixture with tallow lowers the melting point (53°-56° C.). Foreign matter may be detected by boiling with a solvent. Starch which has been found to form 20 to 25 per cent. of commercial samples may be rapidly detected by moistening the freshly cut surface of the wax with iodine solution.

TABLE L.¹

	Specific Gravity.	Iodine Value.	Iodine Value of Fatty Acids.	Saponification Value.	Unsaponifiable Matter, per cent.	Free Acid.
Cod Oil, . . .	9299-9342	162.6-172.7	130-170	186.1-189.5	6-1.5	8-20
Shark Oil, . . .	9105-9177	90-136	...	146-163	19-29	do.
Seal Oil, . . .	9237-9267	142.4-162.6	...	190.0	2-5	do.
Whale Oil, . . .	9162-9272	116-136	130-132	183-188	1.4-3.3	do.
Menhaden Oil, . . .	9270-9311	147-172	...	188.7-192	5-5.0	do.
Tallow, Beef, . . .	945-952	46-55	40	193-200	0.5-1.0	...
Neatsfoot Oil, . . .	9152-9174	66-76	62-65	194-197	do.	...
Olive Oil, . . .	9140-9200	81-85	86-90	185-196	0.7-1.0	1-5
Castor Oil, . . .	9600-9679	83-86	87-93	183-186	0.0-0.5	1-5
Linseed Oil, . . .	9316-9410	173-201	179-182	190-192	0.5-1.0	...
Beeswax, . . .	9590-9700	8-10	...	85-100	...	18-22
Carnauba Wax, . . .	8500-9990	13.5	...	79-83	...	4-7
Japan Wax, . . .	998-1022	4.2-11.3	...	214-222	1.1-1.6	...

Dé gras.—*Specific Gravity.*—This is very difficult to take. It has been proposed to extract the grease with petroleum ether, remove undissolved soaps and tissue fragments by filtration, evaporate the solvent, and take the gravity of the fat in the ordinary way. Ether would be preferable to petroleum for this purpose. The following method is due to Gawalowski (*Collegium*, 1903, p. 5):—An Erlenmeyer flask of 100 c.c. capacity and with a ground top is covered with a glass plate and weighed. It is then about two-thirds filled with the dried dé gras and weighed. Then the flask is kept for a couple of hours at a temperature of about 60°-80° C., and subsequently water is poured into the flask till it is nearly three-quarters full and is gently warmed till no more ebullition takes place. The flask is then cooled, filled with water to the rim, the glass plate put on, and weighed. The water content of the pycnometer flask must be previously determined. The specific gravity is calculated from the following formula:—

$$\frac{(T+D)-T}{[(W+T)-T]-[(W^1+D)-T]-[(D+T)]}$$

Where T = weight of flask.
 T + W = flask filled with water.
 D = weight of dé gras.
 W¹ = weight of water added to fill flask after boiling.

¹ For details of other oils, Lewkowitch's *Laboratory Companion to Fats and Oils Industries* should be consulted.

Determination of Water (Fahrión's method).—About 1 gm. of the dégras is slowly heated in a platinum dish over a small flame with constant stirring until a slight crackling sound and fuming shows that all the water has been expelled. The estimation should be done in duplicate. This method gives accurate results with artificial dégras containing less than 20 per cent. of water. For natural dégras containing more water, 10 grms. should be added to 10 grms. of pure dry sand in a weighed dish and heated in an oven at 120° until constant. According to Jean, asbestos may be advantageously substituted for sand.

Mineral Matter (Ash).—Two to three grms. weighed out exactly into a platinum dish or crucible may be ashed in the ordinary way, beginning with a small flame. To avoid frothing, Jean weighs out about 10 grms. into a platinum dish, stands in the dégras an ashless filter paper folded into a cone, and warms the dish until the dégras oil burns at the apex of the cone as on a wick. Incineration is continued in the usual way until the ash is white. A heavy ash may indicate soap, and its alkalinity should then be determined.

Total Impurities.—When a qualitative test has shown that the dégras contains much matter insoluble in petrol, a quantitative determination should be made of matter insoluble in organic solvents. Ten grms. of dégras previously dried is digested with petroleum ether (boiling below 75° C.), filtered through a tared filter and the residue washed with petroleum ether several times and then with sulphuric ether, or better, with benzine, carbon bisulphate or carbon tetrachloride, to remove oxidised fatty acids. The filter paper and residue is dried and weighed. The weight of matter insoluble in petrol having been so determined, it should finally be ashed and the weight of the ash deducted from the total foreign matter.

Free Fatty Acids.—These may be estimated either in the dry residue obtained in the estimation of water, or in the ethereal extract and washings from the determination of insoluble matter. In the one case digest and stir the residue with 50 c.c. neutral alcohol and titrate with phenolphthalein and $\frac{N}{10}$ alcoholic potash. From the ethereal extract the ether should be distilled off, the residue dissolved in neutral alcohol and titrated.

Total Unsaponifiable Matter.—This may be determined in the usual way, as already described. Baldracco (*Collegium*, 1904, p. 333) saponifies 15 to 20 grms. of dégras with alcoholic potash, distils off most of the alcohol, and pours into 8 grms. of sodium bicarbonate contained in a dish. Fifty to 60 grms. of washed ignited sand are added, and the mixture well stirred and dried. The dry mass is broken up and extracted with petroleum ether in a Soxhlet extractor. Jean employs a quicker method. He heats 10 grms. of dégras in a nickel dish with constant stirring until fuming begins, then adds 4 c.c. of caustic soda (34–40° Bé) mixed with 2.5 c.c. of

alcohol, and heats with constant stirring until the mass is dry. This is dissolved in water, and the mixture extracted twice with ether in a separating funnel by successive inversions of the vessel, to avoid the formation of an emulsion. The ethereal extract is poured into a glass dish 7.5 cm. by 2.5 cm. and evaporated directly in the oven. So evaporated, there is no loss by "creeping."

The total unsaponifiable matter is separable into that which is soluble in alcohol, and the heavy hydrocarbons, which are not. Resins, resin oils, and cholesterol will dissolve in hot spirit, leaving any mineral oil as a residue.

Déragene.—The oxyacids present in dégras are of two kinds, according as their soaps are precipitated or not by common salt. If, after saponifying, removing unsaponifiable matter and ether, salt be added to the soap solution, the soaps of the slightly oxidised oxyjeconic acids will be precipitated, but those of highly oxidised oxyjeconic acids, having lost the characteristic properties of soaps, will remain in solution. By adding salt to the soap solution, filtering, and acidifying the filtrate, the highly oxidised acids may be separated. They are the "resinoid matter" of Jean.

Simmon and Fahrion class as déragene the total oxyacids and anhydrides contained in moellon or dégras. The method of their extraction, depending on their insolubility in petroleum ether, has already been described above. The value of a sample of dégras is directly proportional to the percentage of oxidised acids, since it is to these bodies that the property of emulsifying with water is due.

Suintine or wool-grease may be approximately estimated by Simaud's method. The ethereal solution of fatty acids from 5 grms. of dégras is evaporated in a weighed flask, the residue heated with $1\frac{1}{2}$ parts of acetic anhydride, and the product washed, dried, and dissolved in 15 times its weight of hot alcohol. On cooling, cholesterol acetate crystallises out, and is separated and crystallised twice from 15 parts of alcohol; the pure crystals are dissolved in ether, the ether distilled off, and the residue weighed. Wool-fat gives about 34 per cent. of cholesterol acetate, but the proportion is variable.

According to Simaud, wool-grease may be recognised by the shiny surface of the solid fat, or, if liquid, by the shiny, non-crystalline surface of the separated fatty acids. A useful indication of the presence of wool-grease is its characteristic smell, noticeable when a sample containing it is rubbed between the hands.

Mineral Acids.—A quantity of the oil is boiled with distilled water with stirring. It is then kept on a water-bath till the water has completely evaporated, when it is filtered through a wet ribbed filter in the same way as the fatty acids in the analysis of soap. The filtrate is tested with methyl-orange or litmus and, if acid, titrated. If preferred, the oil may be shaken with hot water in a separating funnel.

The following is an analysis of best light press sod oil, by Schorlemmer:—

TABLE LI.

Water,	17.1	Nitrogen,	0.13
Ash,	0.5	Hide substance,	0.75
Matter insoluble in petrol,	0.1		
Saponifiable fat,	80.4		
Unsaponifiable fat,	1.9		
	100.0		

Constants of the matter soluble in petrol :—

Saponification value,	219.7
Acid value,	22.5
Iodine value,	65.7
Oxidised fatty acids per cent.,	40.1

Dégras frequently contains tallow, and often blown oils of both animal and vegetable origin. So long, however, as the oxidised fatty acids are sufficiently high, viz., not less than 12 per cent. on a basis of 20 per cent. of water, it does not appear to matter very much.

Wool-fat, like dégras, has the power of emulsifying with water, and is sometimes used for the adulteration of true dégras. Since it is very difficult to saponify wool-fat with ordinary alcoholic potash, it will always raise the quantity of unsaponifiable matter present; and if this be resaponified with alcoholic potash in a closed flask and then titrated, a blank being also done, any absorption of potash would point to the presence of wool-grease.

Fat Liquors are generally prepared by the user. Bought samples may be examined on the lines of dégras analysis, determining water, fat, and soap. A known weight or volume of the well-shaken liquor is mixed with sand and dried in the oven. The dry mass is extracted with petroleum ether. The extract, containing the free fat and probably a little soap, is washed several times with distilled water to remove the soap, the washings being kept. The petrol is distilled off and the residue of fat weighed. The bulk of the soap still in the sand is extracted with alcohol, the washings from the petrol extract added, and the fatty acids liberated with acid and weighed. The fat may be further examined to determine its iodine value, unsaponifiable matter, etc.; but the kind of fat is not of great importance so long as the liquor is a good and permanent emulsion. Neutrality, however, is necessary, although in this case an acid leather will precipitate the fat liquor as a greasy mass, while presence of soluble chromium salts will produce irremovable chromium soaps.

Egg Yolk.—This is an expensive substance and liable to sophistication or to be deficient in its most important constituent, egg oil. The analysis of egg yolk includes the determination of moisture, oil, ash, together with a qualitative or quantitative examination of the last two constituents.

Water.—From 15 to 30^{grs} grms. of the sample are weighed out into a

flat-bottomed basin tared together with a little dry sand and a small glass rod. The mixture is heated cautiously at first, and well stirred so as to break up all lumps; it is afterwards dried at a temperature of 100°–105° C. to constant weight.

Fat.—The dry residue is extracted in a Soxhlet apparatus with petroleum spirit (b. pt. 70°–75° C.). When the ether which syphons over is colourless, the residue is withdrawn from the apparatus, dried, powdered, and extracted for a further period. The extract is evaporated, and the residue dried for 1 hour at 100°–105° C. before being weighed. Should the sample contain boric acid, a portion will remain in the fat, and its quantity must be determined and allowed for. The fat is tested qualitatively for boric acid as follows:—About 0.5 gm. is agitated with warm methylated spirit. This is decanted off, acidified and ignited, and the green flame looked for. If present, 2 grms. of the fat are dissolved in petrol and washed in a separator three times with distilled water at 30° C. The three washings are added together, one-third of their volume of pure neutral glycerine added, and the boric acid titrated with decinormal soda and phenolphthalein until a pink colour is just permanent. Each cubic centimetre of decinormal soda is equivalent to 0.0062 gm. of boric acid. The quantity of boric acid thus found must be deducted from the fat.

Sodium Chloride.—The residue insoluble in petroleum spirit is dried, dissolved in water, the volume diluted to 250 c.c., and the chlorine titrated in a known volume of the solution with decinormal silver nitrate solution, using potassium chromate as indicator.

Ash.—Ten grms. of the sample are placed in a platinum basin, dried, and carbonised at a low temperature. The mass is extracted with water, and the extracts evaporated in a weighed basin, whilst the carbonaceous residue is burnt to a white ash, which is added to the extract in the basin. When dry, the whole is heated for some time at a temperature of 100°–105° C. before weighing.

A difference of more than 1.5 between the percentage amounts of sodium chloride and total ash, points to the presence of boric acid or other added mineral matter.

According to Jean, the percentage of egg oil extracted depends largely on the solvent used. Petroleum ether extracts the least. He gives the following figures:—

TABLE LII.

Solvent.	Oil extracted.
Petroleum ether,	48.24 per cent.
Carbon bisulphide or carbon tetrachloride,	50.45 „
Ethyl ether,	50.83 „
Chloroform,	57.66 „

In view of these facts, it is advisable that the solvent used be stated in the report of an analysis.

Determination of Total Boric Acid.—About 10 grms. of the oil are

made alkaline and ashed, dissolved in dilute hydrochloric acid, and heated as described on p. 74.

Characteristics of Egg Oil.—The dry oil should be tested to ensure its purity. Lewkowitzsch gives the following constants:—

TABLE LIII.

Specific gravity,	9144-9156
Solidifying point,	8°-10° C.
Saponification value,	184.4-190.2
Iodine value,	68.5-81.6
Refractive index,	1.4713
Melting-point of the mixed fatty acids,	34.5°-36° C.
Iodine value of mixed fatty acids,	72.6-73.25

Skin Grease.—The grease, obtained either by boiling the skin waste with water and skimming off the melted fat, or by extracting the material with solvents, is a valuable by-product of leather manufacture. It is often sold on a guarantee of 98 per cent. of saponifiable matter, i.e. the difference between 100 per cent. and the sum of the water, ash, and unsaponifiable matter found by analysis. The total fatty matter may be determined directly by heating a weighed quantity on the water-bath with a few drops of strong hydrochloric acid with frequent agitation to decompose lime soaps. Petroleum ether is then added, and the dissolved grease decanted through a tared filter into a weighed flask, the whole of the fat being gradually washed in and the filter paper rinsed with petroleum ether. On evaporating the petroleum, the fatty matter may be directly weighed as well as the insoluble matter on the filter paper. If these two be weighed and the ash also determined, the moisture may be determined by difference. The total fatty matter so determined includes, of course, unsaponifiable. But since the saponifiable matter may include a quantity of lime soap which depreciates the value of grease for soap-making, soap-boilers are beginning to demand stricter analysis and a minimum of lime soap. Grease extracted with solvents is usually almost free from this and other matter insoluble in petrol. Rendered grease always contains appreciable quantities, and should be more fully analysed. Analysis should include estimation of moisture, matter insoluble in petrol, unsaponifiable matter, total fatty acids, and their titer. If the matter insoluble in petrol be much, it should be ashed and the lime in the ash determined to arrive at the amount of lime soap present.

Determination of Benzene.—All benzene recovered greases are liable to contain traces of the solvent, which should never exceed 0.5 per cent. in amount. It may be separated and estimated by weighing 100 grms. of the grease into a large distilling flask connected with a worm condenser. A rapid current of steam is then passed through, the distillate being collected in a flask with a long graduated neck, in which the volume of benzene may be read off. It is sometimes desirable to use superheated

steam. In this case a furnace containing an iron tube is placed between the boiler and the distilling flask, the latter being immersed in an oil-bath kept at the desired temperature.

Glycerine.—The percentage of glycerol present in an approximately pure sample may be deduced either from the specific gravity or the refractive index. The following table by Lenz gives the relation between these contained and the percentage of glycerol:—

Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12.5°-12.8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12.5°-12.8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12.5°-12.8° C.
Per cent.			Per cent.			Per cent.		
100	1.2691	1.4758	66	1.1764	1.4249	32	1.0825	1.3745
99	1.2664	1.4744	65	1.1733	1.4231	31	1.0798	1.3732
98	1.2637	1.4729	64	1.1702	1.4213	30	1.0771	1.3719
97	1.2610	1.4715	63	1.1671	1.4195	29	1.0744	1.3706
96	1.2584	1.4700	62	1.1640	1.4176	28	1.0718	1.3692
95	1.2557	1.4686	61	1.1610	1.4158	27	1.0699	1.3679
94	1.2531	1.4671	60	1.1582	1.4140	26	1.0683	1.3666
93	1.2504	1.4657	59	1.1556	1.4126	25	1.0665	1.3652
92	1.2478	1.4642	58	1.1530	1.4114	24	1.0698	1.3639
91	1.2451	1.4628	57	1.1505	1.4102	23	1.0580	1.3626
90	1.2425	1.4613	56	1.1480	1.4091	22	1.0553	1.3612
89	1.2398	1.4598	55	1.1455	1.4079	21	1.0525	1.3599
88	1.2372	1.4584	54	1.1430	1.4065	20	1.0498	1.3585
87	1.2345	1.4569	53	1.1403	1.4051	19	1.0471	1.3572
86	1.2318	1.4555	52	1.1375	1.4036	18	1.0446	1.3559
85	1.2292	1.4540	51	1.1348	1.4022	17	1.0422	1.3546
84	1.2265	1.4525	50	1.1320	1.4007	16	1.0398	1.3533
83	1.2238	1.4511	49	1.1293	1.3993	15	1.0374	1.3520
82	1.2212	1.4496	48	1.1265	1.3979	14	1.0349	1.3507
81	1.2185	1.4482	47	1.1238	1.3964	13	1.0322	1.3494
80	1.2159	1.4467	46	1.1210	1.3950	12	1.0297	1.3480
79	1.2122	1.4453	45	1.1183	1.3935	11	1.0271	1.3467
78	1.2106	1.4438	44	1.1155	1.3921	10	1.0245	1.3454
77	1.2079	1.4424	43	1.1127	1.3906	9	1.0221	1.3442
76	1.2042	1.4409	42	1.1100	1.3890	8	1.0196	1.3430
75	1.2016	1.4395	41	1.1072	1.3875	7	1.0172	1.3417
74	1.1999	1.4380	40	1.1045	1.3860	6	1.0147	1.3405
73	1.1973	1.4366	39	1.1017	1.3844	5	1.0123	1.3392
72	1.1945	1.4352	38	1.0989	1.3829	4	1.0098	1.3380
71	1.1918	1.4337	37	1.0962	1.3813	3	1.0074	1.3367
70	1.1889	1.4321	36	1.0934	1.3798	2	1.0049	1.3355
69	1.1858	1.4304	35	1.0907	1.3785	1	1.0025	1.3342
68	1.1828	1.4288	34	1.0880	1.3772			
67	1.1795	1.4267	33	1.0852	1.3758			

At 15.5° C. the relation between specific gravity and percentage of glycerine becomes—

Glycerol.	Specific Gravity at 15.5° C.	Glycerol.	Specific Gravity at 15.5° C.
Per cent.		Per cent.	
100	1.2674	87	1.2327
99	1.2647	86	1.2301
98	1.2620	85	1.2274
97	1.2594	84	1.2248
96	1.2567	83	1.2222
95	1.2540	82	1.2196
94	1.2513	81	1.2169
93	1.2486	80	1.2143
92	1.2460	79	1.2117
91	1.2433	78	1.2090
90	1.2406	77	1.2064
89	1.2380	76	1.2037
88	1.2353	75	1.2011

Lewkowitsch recommends the following method of taking the specific gravity:—The sample is warmed in water until all enclosed air bubbles have escaped. After cooling carefully it is poured into an ordinary specific gravity bottle, pushing the stopper well down.

Of chemical methods for the estimation of glycerol, that known as the *Acetin Method* is the only reliable one—in which the glycerine is transformed into triacetin and the amount of standard caustic alkali necessary for its saponification is measured, and from this the equivalent of glycerine is calculated. The experiment is carried out as follows:—About 1.5 grms. of the glycerine are placed in a small flask, together with 3 grms. of dried and gently ignited sodium acetate, and 7 to 8 c.c. of acetic anhydride. The flask is then placed on a sand-bath beneath an inverted condenser and gently boiled for about 2 hours, to convert the glycerine into triacetin. After cooling, about 50 c.c. of water are carefully poured into the flask through the condenser, and the contents gently agitated or warmed till the whole is dissolved. It is better to avoid warming if possible, as triacetin is very volatile. The solution is next filtered into a large flask of about a litre capacity, the residue of insoluble matter being washed with water. To the cool filtrate a little phenolphthalein is added and the free acetic acid neutralised by the careful addition of 20 per cent. caustic soda. Great care must be taken in this operation not to add excess of soda, as it will at once saponify some of the triacetin. The change of colour from yellow to red is very distinct, but exact neutralisation is best obtained by completing the titration with decinormal soda. When the acetic acid is neutralised, exactly 25 c.c. of 10 per cent. caustic soda solution are added to the flask, and the mixture boiled for about 15 minutes. At the same time a second 25 c.c. of the soda solution is diluted to a similar volume and boiled. After boiling, both solutions are cooled and titrated with seminormal hydrochloric acid.

The difference between the volumes required by the flask and the sample gives the amount of soda used in the saponification of the triacetin, each c.c. of seminormal soda, 0.0153 grms. of glycerol.

Other tests of purity include:—

Ash.—From 3 to 5 grms. are carefully incinerated over a bunsen flame till a charred mass is obtained, care being taken not to heat sufficiently to expel sodium chloride. The charred mass is cooled, extracted with water, and filtered. The carbon residue is then dried and burnt in a platinum dish, the filtrate obtained above being subsequently added, and the whole evaporated to dryness on the water-bath, gently ignited, and weighed. *Sugar and organic impurities* will be detected by the usual tests. Arsenic may be estimated electrically, an acidified solution of the sample being introduced directly into the inner cell of the apparatus. Organic impurities such as polyglycerols may be determined by evaporating a weighed quantity at 160° C., adding every now and then a few drops of water. The residue which remains after deducting the ash is due to organic impurities. A commercially pure glycerine should never give more than 0.1–0.2 per cent. of residue at 160° C.

CHAPTER XIV.

SOAP.

SOAP should invariably be bought upon analysis, and there are few articles in use in a tannery which are subject to such variation in quality. The work which soap will do depends entirely on the percentage of fatty acids present, and these in a good soap should never be less than 62 to 63 per cent. Again, for many purposes the absence of free alkali is of importance, as also is the nature of the fat from which the soap was prepared, and a knowledge of the presence or absence of resin acids. The following is an outline of the methods to be employed in the examination of soaps:—

Sampling.—Solid soaps should be sampled by cutting a slice right through the bar. If the sample be taken from the middle, the percentage of water will be undoubtedly high, while the outer layers will similarly be over dry.

Determination of Water.—This is not of great importance, since, the other constituents having been determined, the water contained follows as a matter of course by difference. It may be directly determined in two ways:—

1. About 5 grms. of the soap are cut into very fine shavings and weighed in a flat dish. This is dried for some time at a low temperature, not exceeding 40° to 50° C., in order to prevent the soap from melting. It is then dried to constant weight in an air-oven at 105° C.

- 2 The finely-divided soap is weighed in a porcelain or nickel dish with a glass stirring-rod, and carefully heated on a sand-bath with constant stirring until no water is expelled. This method is rapid, but not very accurate, since it is extremely difficult to prevent the soap from burning.

Estimation of Free Fat.—The dried soap obtained as above is extracted in a Soxhlet apparatus with petroleum ether in the usual way.

Since soap is distinctly soluble in petrol, the solution of the fat must be thoroughly washed before evaporating. To remove the last traces of soap, it is sometimes well to redissolve the residue obtained in petrol and wash again once or twice. In the absence of soaps, the weight will of course be unchanged by this second washing. If necessary, the fat may be saponified and the proportion of unsaponifiable matter determined.

Determination of Fatty Acids and Total Alkali.—About 10 grms. of the soap are dissolved in distilled water, and when solution is complete titrated with normal acid and methyl orange, each cubic centimetre of acid used being equivalent to 0.031 gm. of sodium oxide (Na_2O). The acids having been liberated, the beaker is placed upon the water-bath and heated until a perfectly clear layer of fatty acids is obtained. A ribbed filter is then placed in a funnel and wetted with hot water and the mixture rapidly filtered, care being taken to prevent the fatty acids from solidifying on the filter-paper during the process. The fatty acids will remain upon the filter-paper and can be washed with hot distilled water until free from mineral acid. They are then dissolved off the paper with warm spirit, being allowed to run into a flat weighed glass dish. The alcohol is evaporated off on the water-bath and the residue weighed. Instead of titrating the total alkali directly, an excess of normal acid may be added and the unused portion titrated back in the filtrate from the fatty acids. If preferred, the soap solution may be decomposed in a separating funnel in the presence of ether, and the ethereal layer separated and evaporated in a weighed flask. Petroleum ether must not be used, since resin acids are not all soluble in it. A rapid method of analysis with ether is to decompose the soap solution in a graduated cylinder, extract with ether, and pipette off an aliquot portion of the ethereal solution for evaporation. The following method is rapid, but approximate only in results. From 10 to 20 grms. of the soap are dissolved in distilled water in a beaker and the fatty acids liberated as before. A weighed quantity of beeswax is now added, and the heating continued until it is completely melted and mixed with fatty acids. The beaker is now cooled, when the fatty acids and beeswax form a hard cake, which can readily be removed, allowed to drain on a filter-paper and weighed. The weight of the beeswax is, of course, deducted from the total weight.

Insoluble Matter.—If much insoluble matter be present, such as silica, it will be observed as a precipitate upon liberation of the fatty acids, and, after dissolving the latter from the filter-paper with alcohol, will be left behind. The paper may be incinerated and the residue weighed. If, however, silica and other insoluble matter be found to be present, it is better to determine them in the ash.

Determination of Combined and Free Alkali.—The fat-free soap obtained as above is dissolved in absolute alcohol and filtered into a 250 c.c. flask, the filter-paper being rapidly washed with hot alcohol until the whole of the soap has been removed. If preferred, the operation may be carried out in a Soxhlet extractor. The residue on the filter-paper will consist of carbonates, borates, and other mineral substances, together with starch and certain organic matters, if present. The solution will contain the soap and any free caustic alkali that may be present. A few drops of phenolphthalein are added, and caustic alkali, if present, is titrated with decinormal acid, after which the solution is made up to 250 c.c., a portion of it with-

drawn, diluted considerably with water, and the combined alkali titrated with decinormal acid and methyl orange. It is important to remember that methyl orange is not sensitive in strong alcoholic solutions, hence the necessity for dilution. For the determination of free carbonates the residue on the filter-paper is dissolved in water and titrated with standard acid and methyl orange. Each c.c. of decinormal acid used will correspond to .0053 gm. of dry sodium carbonate.

The Testing of Fatty Acids.—The fatty acids obtained above should be tested for resin acids as follows:—About 1 gm. of the fatty acids is warmed with acetic anhydride and afterwards cooled. The clear liquid is then poured into a porcelain dish and a drop of strong sulphuric acid added, when, in the presence of resin acids, a violet coloration is obtained. If present, the percentage of resin acids may be determined by Twitchell's method, which depends upon the fact that the fatty acids are converted into ethers when treated with hydrochloric acid gas, while the resin acids remain unchanged. About 3 grms. of the mixed fatty acids are dissolved in 10 times their volume of absolute alcohol and subjected to a rapid stream of hydrochloric acid gas. This is conveniently prepared by allowing strong sulphuric acid to drop from a tap funnel into a flask (fig. 37) containing

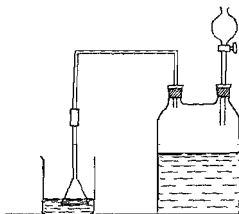


FIG. 37.

hydrochloric acid. The solution of the fatty acid should be placed in a beaker, and the delivery tube connected with a filter funnel which dips beneath the surface to the liquid, in order to prevent it being sucked back by absorption. During the absorption the beaker should be cooled with water. When no more gas is absorbed, the beaker is covered and allowed to stand for an hour, after which 5 volumes of distilled water and the contents of the beaker are boiled until the solution

has become clear. The liquid is then run into a separating funnel and the beaker washed out with ether, and the whole shaken with the same liquid. The ether layer is washed with water and then treated in the funnel with 50 c.c. of a 1 per cent. solution of caustic potash and 5 c.c. of alcohol. This will convert the resin into soaps, which will be dissolved in the lower layer, the fatty esters remaining dissolved in the ethereal layer; the soap solution is run off, decomposed with hydrochloric acid, and the resin acids shaken out with ether and weighed.

Examination of Fatty Acids.—The ethereal solution of the fat acids is placed in a flask, the solvent driven off and the ethers saponified with alcohol potash. The alcohol is then evaporated, the soap dissolved in water, and the fatty acids liberated and separated as described above.

They may then be tested as required. If regularity of action is desired it will, of course, be of importance to see that the fatty acids have fairly constant properties. This is best seen from the determination of the iodine value, saponification equivalent, or, perhaps, more readily from the

TABLE LIV.

Titer Tests of Mixed Fatty Acids (Lorkowitsch).

Class of Fat.	Kind of Fat.	Titer Test.	Remarks.
Vegetable fats.	Cotton seed stearine.	84.9 - 35.1	
	Chaulmoogra oil.	39.5 - 39.6	
	Laurel oil.	14.3 - 15.1	
	Mowrah seed oil.	38.3 - 38.5	
	Shea butter.	53.75 - 53.8	
	Vegetable tallow. ¹	52.1 - 53.4	
	Palm oil, Bonny.	35.8 - 35.9	
	" Bassam.	38.0 - 38.47	
	" Lagos.	43.8 - 43.925	
	" Old Calabar.	44.3 - 44.6	
	" Salt Pond.	44.3 - 44.475	
	" New Calabar.	45.4 - 45.55	
	" Congo.	44.9 - 45.05	
	Macassar oil.	51.8 - 53.2	
	Sawarri fat.	46.0 - 47.0	
	Nutmeg butter.	35.5 - 35.95	
	Cacao butter.	48.0 - 48.27	
Palm nut oil.	20.0 - 20.5	Lowest.	
" "	24.6 - 25.5	Highest.	
Cocoa nut oil, commercial.	21.2 - 22.55	Lowest.	
" "	24.8 - 25.2	Highest.	
" Cochin.	24.8 - 25.2		
Japan wax.	58.8 - 59.4		
Animal fats.	Horse fat.	33.6 - 33.7	
	Horse marrow.	38.4 - 38.55	
	Lard.	41.45 - 42.0	
	Beef tallow, English.	38.45 - 38.7	Lowest.
	" "	45.0 - 45.1	Highest.
	" " North American.	38.9 - 41.1	Lowest.
	" " "	43.3 - 44.15	Highest.
	" " South American.	42.75 - 42.95	Lowest.
	" " "	45.7 - 46.25	Highest.
	" " Australian.	37.9 - 38.3	Lowest.
	" " "	43.05 - 43.3	Highest.
	Mutton tallow, English.	40.15 - 41.5	Lowest.
	" " "	47.5 - 48.3	Highest.
	" " Australian.	41.65 - 42.35	Lowest.
" " "	47.8 - 48.05	Highest.	
Beef marrow.	37.9 - 38.0		

¹ Commercial.

titer test, by which is meant the solidification point of the fatty acids. This test is carried out as follows:—A sufficient quantity of the fatty acids are dried in a desiccator and poured into a wide test tube (6 cm. long and 3.5 cm. wide) until the tube is about half full. The tube is

then immersed in cold water and a delicate thermometer placed in the melted fatty acid. The contents of the tube are now allowed to cool until a few crystals are found at the bottom of the tube, when the mass is stirred by means of the thermometer without allowing it to touch the sides of the tube, in such a way that the solidified portions are completely mixed with the rest of the mass. The temperature will for a time continue to fall, but finally it will suddenly rise a little and remain stationary for a little while. This stationary temperature is known as the titer. According to Lewkowitsch the titer test gives reliable results for the commercial valuation of fats, and the preceding table on page 215 is given by him.

Full details of the constants of the oils used in soap-making will be found in Lewkowitsch's *Laboratory Companion to Fats and Oils Industries*.

Determination of Glycerine.—Fifty grms. of the soap are dissolved in water and made faintly acid with hydrochloric acid, and the liberated fatty acids filtered off, returning the filtrate till it is quite clear. The filtrate is neutralised with lead acetate and concentrated, the salt being collected as it separates, and thrown on to a perforated filter plate attached to a pump. When only a few cubic centimetres are left, the liquor is also filtered through the plate, the salt being extracted with a mixture of three parts of alcohol and one of ether. These washings are added to the residual mother liquor, and the whole evaporated in a small flask on the water-bath, and the glycerine determined in the residue by the acetin method. This process is also suitable for fat liquors. If preferred, the filtrate from the fatty acids may be neutralised with barium carbonate, and after concentration, evaporated to dryness on the water-bath; the residue is extracted with alcohol and ether as described above.

CHAPTER XV.

VARNISHES.

THE analysis of varnishes presents much difficulty, since their composition is so varied. The first step in the analysis of a varnish is to determine the nature of the solvent, since, if this should prove to be water, a great many possible constituents are at once excluded. For the detection of the solvent a considerable quantity of the varnish is distilled in a current of steam. If spirit be present it will be found in solution in the distillate, while immiscible solvents can be separated by means of a separating funnel, and tested, after drying, for calcium chloride by means of specific gravity and other tests. Obviously no very general method of analysis can be given. The same statement applies to the residue in the flask. In general, however, it may be examined for insoluble matter thrown out of solution by the loss of organic solvents. This may be filtered off and examined. The filtrate should then be shaken with ether in a separating funnel, and, after removing the ethereal layer for further examination, shaken again in the presence of acid in order to decompose any soaps which may be present and separate their fatty acids. A further portion of the varnish should be boiled with acid and filtered for the detection of coagulable albuminoids, which are frequently present. The mineral matters present may, of course, be determined in the ash. In connection with leather varnishes the chief constituents appear to be soaps, algin, and similar bodies, and sometimes collodion. Soaps are sometimes present as sodium compounds, but more often as those of the alkaline earths, which, although insoluble in water, are soluble in a number of organic solvents, such as benzine, petroleum, and turpentine. Hence they can be detected by evaporating to dryness and extracting the residue with one of these liquids. The resinates are also frequently used. After acidification, resin acids can be extracted by means of ether and easily recognised by the usual test.

Algin is soluble in water and precipitated by acids and many other substances, but not by tannin or magnesium chloride. If it be estimated it may be separated by boiling with dilute acid and filtering and washing the precipitate with alcohol till free from acid. The precipitate is then

boiled with a solution of dilute sodium carbonate and filtered. On acidifying with hydrochloric acid the alginic acid is thrown down. It is then dissolved in water and tested. If neutralised with sodium hydrate or carbonate the solution is not coagulated on boiling, and yields no precipitate with potassium ferrocyanide or aënic acid. These tests distinguish it from albumin. It may be distinguished from agar, a similar body also prepared from seaweed, by the fact that it contains nitrogen and does not gelatinise on cooling. It differs from dextrin, gum arabic, and gum tragacanth by being thrown down by dilute alcohol and mineral acids. If tragacanth be present the varnish also generally contains borax. The gum may be precipitated by means of alcohol or warming with lead acetate. Collodion will be thrown down on diluting with water. It may be filtered off, washed with alcohol, and dissolved in a mixture of alcohol and ether. A little of the solution is then run into a nitrometer tube filled with mercury, followed by a little strong sulphuric acid. The air having been driven out by adjusting the level of the mercury, the tube is shaken so as to bring the mixture into contact with the metal, when nitric oxide will be liberated. This may be identified by washing in a little ferrous sulphate solution, which will dissolve the nitric oxide and at the same time turn black.

Other common ingredients of varnishes are carbon, Prussian blue, shellac, etc. If a varnish be boiled with alcoholic potash and the undissolved residue heated with hydrochloric acid, the insoluble matter will contain any carbon present and it may be approximately estimated by drying, weighing and ashing, and deducting the weight of the ash.

CHAPTER XVI.

SKIN.

Structure.—The skins of mammals consist of two portions, the *epidermis* and the *dermis*. The epidermis belongs to that class of tissues known as “stratified epithelia.” A stratified epithelium is composed of layers of cells, in which the cells gradually become more and more flattened the nearer they come to the surface of the tissue. The flattening of the cells is accompanied by a gradual change in chemical composition, until the whole of the protoplasm of the cell is transformed into a horny substance. As these cells wear away they are replaced by others which are formed by the continuous division of the cells of the lower layers, so that the cells which originally belonged to the lowest layers gradually work their way to the surface; at the same time they change from ordinary into flat-horny cells (*H*, fig. 38). The function of the epidermis is to form a protective covering for the dermis, or true skin. It may be divided into two distinct parts—(1) An outer horny layer, the *stratum corneum* (*H*, fig. 38); (2) an inner soft layer, the *Malpighian layer* (*M*, fig. 38). These two layers are separated by a fairly well-defined stratum known as the *stratum granulosum* (*s.gr.*, fig. 38). Above this stratum is a layer of elongated flattened cells which are clear and transparent, and hence is called the *stratum lucidum* (*s.l.*, fig. 38). The growth of the epidermis takes place by cell division in the Malpighian layer, the cells of the uppermost layers being thrust up into the *stratum granulosum*, where it is thought the presence of granules have some connection with the production of the keratin.

When this transformation of the cell protoplasm into keratin is complete, the granulated cells are in their turn pushed upwards and gradually reach the surface, where they peel off as flat horny plates. If examined under the microscope they can be no longer identified as cells, the nucleus having entirely disappeared.

The *cutis vera* or *corium* or *true skin* is well supplied with both blood vessels and nerves, and is of an extremely delicate nature; hence the necessity for the protecting epidermis. It is made up of connective tissue mixed with elastic fibres. Projecting from its surface are numerous

papillæ (*BP*, fig. 39). These are most numerous wherever the sense of touch is most delicate, being particularly well developed on the sensitive portions of the hands and feet. Numerous ducts leading from the sweat glands of the connective tissue immediately below the dermis are also to be seen (*D*, fig. 39), as well as hair follicles and sometimes muscular tissue. The sudoriparous canals are lined with nucleated cells and pass through the dermis into the epidermis, where they become simply tubular passages ending in a pore (*P*, fig. 39) at the surface. A knowledge of these pores is

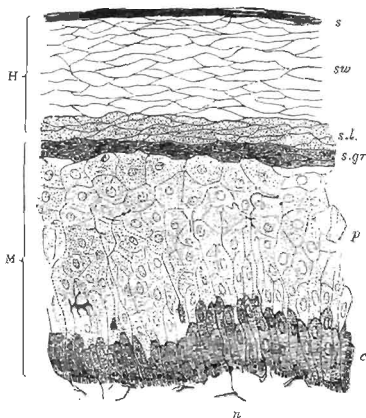


FIG. 38.—Section of Epidermis. (Ranvier.)

H, horny layer, consisting of *s*, superficial horny scales; *sw*, swollen-out horny cells; *s.l.*, stratum lucidum; M, rete mucosum or Malpighian layer, consisting of *p*, prickle-cells, several rows deep; *c*, elongated cells forming a single stratum near the corium; and *s.gr.*, stratum granulosum of Langerhans, just below the stratum lucidum; *n*, part of a plexus of nerve-fibres in the superficial layer of the cutis vera. From this plexus fine varicose nerve-fibrils may be traced passing up between the epithelium cells of the Malpighian layer.

often of use in examining leather. All skin contains numerous hair follicles (*C*, fig. 40), from each of which grows a hair.

Hair follicles are always accompanied by sebaceous glands and adipose tissue. The sebaceous glands consist of small bundles of cells connected by a duct to the follicle. The cells lining the gland gradually become filled with granules and minute drops of fat, and at the same time their nuclei shrink and ultimately disappear, thus indicating that the cell is dying. Finally, when the nucleus has completely broken up, the cell is

shed into the duct, and, disintegrating, forms the secretion known as *sebum*. This process, which is analogous to the production of milk in the mammary glands, is quite distinct from ordinary cell secretion. Immediately beneath the dermis is the subcutaneous and adipose tissue, into which the skin passes without any very definite line of demarcation; hence in removing the skin from an animal a quantity of this tissue is always removed with it. In order to make a microscopic study of the structure of skin, it is, of course, necessary to obtain thin sections cut both vertically and horizontally. In some cases fairly satisfactory horizontal sections may be obtained by cutting with a razor, but for really satisfactory specimens a form of microtome must be employed. The section may be mounted in glycerine and examined, or, if a permanent section be required, it must be

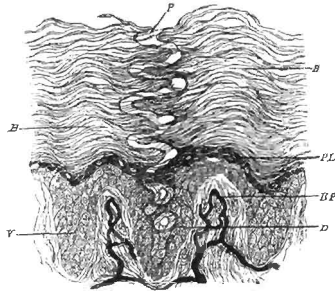


FIG. 30.—Duct of a Sweat-gland passing through the Epidermis.
(Magnified 200 diameters.) (Heitzmann.)

DP, papillæ with blood vessels injected; *V*, rete mucosum between the papillæ; *E*, stratum corneum; *PL*, stratum granulosum; *D*, duct, opening on the surface at *P*.

dehydrated by passing it through alcohol of gradually increasing strength, and finally cleared with clove oil.

Preparation of Permanent Sections.—In order to prepare permanent microscopical sections of tissues, they should first be hardened by placing them for about a week in a suitable hardening agent. The following are generally employed:—

1. *Chromic Acid*.—Made by dissolving 5 grms. in a litre of water. This solution is diluted down to 2 per cent. for use. Chromic acid hardens tissues by tanning them, and if they are left in it too long they are apt to become brittle. A little picric acid may be sometimes added with advantage. This solution is made by adding 2 c.c. of concentrated sulphuric acid to 100 c.c. of a saturated solution of picric acid, filtering, and making the filtrate up to 400 c.c. with distilled water.

2. *Osmic Acid* in a 1 per cent. solution. In making osmic acid solution the water used must be perfectly free from organic matter and the bottle scrupulously clean and preserved from the action of light by means of paraffined brown paper. Osmic acid, in addition to hardening, readily renders visible the nuclei and stains fat cells black.

3. *Alcohol*.—Alcohol may be used by itself or to complete the action of other hardening agents. It makes tissues rapidly opaque by coagulating the albumen. A tissue to be hardened by alcohol alone is first placed in 50 per cent. spirit for a couple of days, then transferred to 75 per cent. alcohol for a few hours, and finally placed in absolute alcohol until

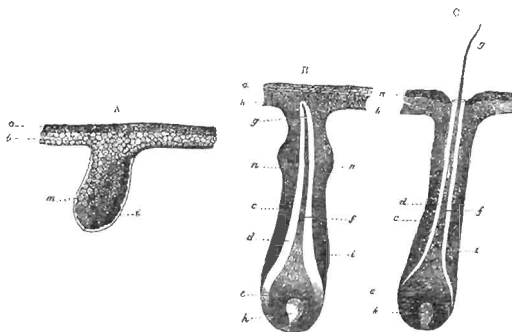


FIG. 40.—Developing Hairs. (From Kölliker.)

A, hair-rudiment from an embryo of six weeks; *a*, horny, and *b*, mucous or Malpighian layer of cuticle; *i*, basement-membrane; *m*, cells, some of which are assuming an oblong figure, which chiefly form the future hair. B, hair-rudiment, with the young hair formed but not yet risen through the cuticle; *a*, horny; *b*, Malpighian layer of epidermis; *c*, outer, *d*, inner, root-sheath; *e*, hair-knob; *f*, stem; and *h*, hair-papilla; *n*, *n*, commencing sebaceous follicles. C, hair-follicle with the hair just protruded.

sufficiently hard. Gradually increasing the strength of the alcohol prevents undue shrinking.

In the case of skin, either chromic acid or a mixture of chromic and osmic acids may be used. When the tissue is sufficiently hardened it is transferred to dilute alcohol, which is changed as long as it abstracts any colour from the tissue, which is then passed through 75 and 100 per cent. alcohol, as described above. It is then carefully dried with filter paper and embedded in paraffin. In the absence of a proper embedding apparatus this may be done as follows:—

Take a small block of paraffin and scoop out a small hole at one end,

and place the tissue in the hole in the required position. Then pour over it a little melted paraffin mixture (paraffin 2 parts, vaseline 1 part). Remove all air bubbles carefully by means of a needle, with which the tissue is also held in its place until the paraffin has solidified. When perfectly cold, cut down the paraffin until the surface of the tissue just appears. Then it will be ready for section cutting. If the sections are cut with a razor it must be very sharp and kept wet with diluted alcohol. If a microtome be used the paraffin block is placed in the holder at the end of the rocker. When a ribbon of sections has been obtained it is floated in a watch-glass of water with the aid of a camel-hair brush, and the thinnest section picked out with a section lifter and transferred to a watch-glass containing a suitable stain, such as picocarmine. After staining, the sections are washed with water and dehydrated by immersion in 50, 75, 90, and 100 per cent. alcohol. They are then cleared by soaking in oil of cloves and mounted in Canada balsam.

A useful and inexpensive form of freezing microtome is shown in the accompanying diagram (fig. 41). Tissues to be cut are soaked in a solution of gum arabic without dehydration. If they have been kept in alcohol they must be soaked in weak alcohol and finally in water before use. The tissue is allowed to remain in the gum solution for some hours. It is then placed on the plate of the microtome, together with some gum solution, and frozen with a spray of ether until quite firm. The solid mass of frozen gum is then trimmed off and the razor adjusted with the levelling screw and wetted with water before cutting. The instrument may equally well be used for tissue embedded in paraffin.



FIG. 41.

Microscopic examination of the stained section.

(1) *The Epidermis*.—Starting from the outside will be seen—

- (a) Non-nucleated horny cells in which the protoplasm has been entirely changed into horny keratin, and which are more and more flattened the nearer they are to the surface.
- (b) Below the horny layer will be seen nucleated spheroidal cells, and beneath these a layer of columnar nucleated perpendicular cells. These two strata together form the Malpighian layer. The gradual transition of the columnar into spheroidal, and ultimately flattened and non-nucleated cells, which are peeled off at the surface, should be specially noted.

(2) *The Dermis*, which consists of the following elements:—

- (a) A thin outer layer of white fibrous tissue containing connective tissue corpuscles and elastic fibres together with a hyaline matrix. The lower portions of this pass gradually into
- (b) The subcutaneous connective tissue; but there is no definite separating line between the two layers. Numerous papillæ will be observed on the subcutaneous tissue.
- (c) *The Papillæ*.—These are conical projections of the dermis into the Malpighian layer.
- (d) Hair follicles and roots of hairs.
- (e) Sebaceous glands, which open into the hair follicle.
- (f) The ducts of sweat glands which pass through the dermis into the epidermis, on the surface of which they terminate as pores. The distribution of sweat glands is, however, as a rule limited to those portions of the skin not covered by hair.
- (g) Numerous blood vessels and bundles of nerves will also be observed, but will in general require special methods of staining.

Analysis of Skins.—The total nitrogen content will give an idea of the proportion of skin substance present. If, however, any putrefaction has taken place, the degraded nitrogenous substances in the form of peptones or lower nitrogen compounds should be first removed by washing with cold water. The following table (Von Schroeder and Paessler, taken from Procter's *Principles of Leather Manufacture*) gives the nitrogen content of various varieties of purified corium:—

TABLE LV.

	Percentage of Nitrogen.
Ox-hide,	18·3
Ox, calf, horse, camel, pig, rhinoceros,	17·8
Goat and deer,	17·4
Cat,	17·1
Sheep and dog,	17·0

For purposes of calculation the percentage of nitrogen is assumed to be 17·8.

Inasmuch as pickled skins sometimes contain materials which are of a very hygroscopic nature, the determination of nitrogen is often important.

The percentage of peptonised nitrogen due to decomposition may be determined by extracting the finely divided skin with cold distilled water and saturating the solution with magnesium sulphate. This will precipitate any dissolved gelatine or albumoses. These are filtered off, and the filtrate is treated with bromine to precipitate the peptones, which are filtered off, and their nitrogen content determined, or the filtrate from the magnesium sulphate precipitate is concentrated and its nitrogen content determined directly.

Arsenic.—It is sometimes necessary to test skins for the presence

of arsenic. In testing for arsenic a weighed portion of the skin is shredded and covered with pure magnesia, dried, and ashed in the muffle. The residue is then dissolved in dilute sulphuric acid, and, after digesting for some time, filtered. To the filtrate is added about 1 grm. of potassium metabisulphite and the mixture boiled till all the sulphur dioxide is expelled. This is to reduce arsenates to arsenites, since the latter are not so readily acted upon by nascent hydrogen. The liquid is then made up to a given volume and an aliquot portion introduced into the inner cell of an electrolytic Marsh's apparatus, and the mirror produced compared with a standard.

CHAPTER XVII.

ANALYSIS OF LEATHER.

Preparation of Sample.—A sufficient quantity must be ground to a fine powder in a mill or by means of a sharp knife or chisel.

Determination of Moisture.—From 5 to 10 grms. of the powdered leather are dried at a temperature of 105° C. until constant in weight. The weighings must be made at frequent intervals, since most of the oils which leather contains readily oxidise upon prolonged heating. When it is necessary to prevent this, the sample must either be dried in a vacuum or in an atmosphere of neutral gas, such as coal gas. Nihoul states that if after 1½ hours the temperature of the drying oven be raised to 120° C., the drying is completed in about half an hour without damage to the leather.

Determination of Fat.—From 20 to 25 grms. of the powdered leather are extracted in a Soxhlet apparatus with petroleum ether. Since the sample will be bulky it is best to put a plug of fat-free cotton wool at the bottom, then the leather, and a plug of cotton wool above it. After the extraction is completed the petrol is distilled off and the residual fat weighed. In cases where oxidisable oils have been used in the leather, the results given will be too low. The extracted oils may be examined, if necessary for identification, by the ordinary methods, such as determination of unsaponifiable matter, iodine value, saponification value, refractive index, etc. Better results (Nihoul, *loc. cit.*) are obtained if a tap separating funnel is used, the stem passing through the cork of a large fat flask which holds the extracting liquid. Some pieces of glass are put in the funnel and then a layer of asbestos, upon which the leather is placed. The funnel is closed at the top by a cork, through which passes the end of a condenser and a tube coiled several times, and passing downwards into the flask through a second hole in the cork. The petrol is distilled from the flask into the separating funnel, the tap being closed and allowed to remain, for some time in contact with the leather. It is then drained off by opening the tap and the operation repeated.

Determination of Total Soluble Matter.—The fat-free residue is placed in a syphon extraction apparatus, as used in the analysis of tanning materials, and treated with water at 40° C., and the extraction carried on

in exactly the same way as for a tanning substance until a litre of extract is obtained. The last washings are collected separately, if necessary, and concentrated before addition to the litre flask. The solution is now filtered through a "candle" filter and 50 c.c. evaporated and weighed for the determination of total soluble matter. Godfrin's extractor (*Collegium*, 1906, 415-416) may be advantageously used.

Godfrin's Extraction Apparatus for Leather (fig. 42).

—Ten grms. of coarsely powdered, dry and fat-free leather are placed in *J* and 30 c.c. of distilled water admitted from *A*. This is enough to wet and swell the leather, but not enough to reach the opening *K*. After 24 hours water is run from *A* drop by drop until *K* is reached, when, for every drop from *A*, another overflows through the capillary tube *E* into the receiver, the flow proceeding automatically and being so regulated as to take about 2 hours for the passage of 500 c.c. of extract.

The extraction is conducted at the temperature of the laboratory, and is so complete that the matter dissolved by a second extraction is negligible.

By placing at the bottom a little wadding and a layer (2 cms.) of sand, a perfectly clear extract was obtained from quebracho.

Estimation of Tannins and Non-Tannins in the Total Soluble Matter.—(*A*) *Free Tannin*.—The solution may be rapidly concentrated by boiling in a large flask until it is sufficiently concentrated to examine by the hide-powder method, or it may be analysed by means of the Löwenthal process. Since boiling is likely to destroy a considerable portion of the tannin in a dilute solution, the Löwenthal method is undoubtedly more suitable. The nature of the free tannin is determined by the qualitative tests already given.

B. Non-tannins.—The difference between the tannin as determined by

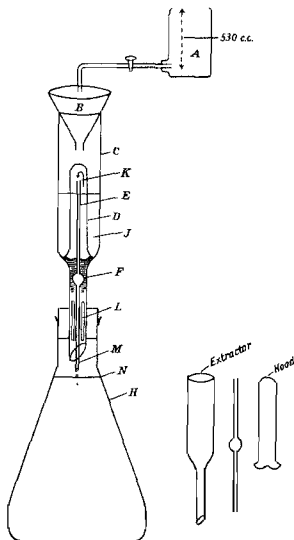


FIG. 42.

the Löwenthal process and the total soluble matter found above will be soluble non-tannins.

Estimation of Hide Substance.—0.5 grm. of the fat-free powder is used, and the methods previously described may be employed. Nihoul recommends .6 to .7 grm. to be boiled for half an hour with 10 c.c. of acid, when it is allowed to cool and a dozen crystals of potassium permanganate added, after which the boiling is continued and the analysis completed in the ordinary way.

From the fact that hide substance contains 17.8 per cent. of nitrogen the percentage present may be calculated by multiplying the percentage of nitrogen by 5.52, or more accurately from the following formula by Bartel (*Dingler's Polyt. J.*, cccv., 65-192; *J.S.C.I.*, 1898, 164):—

From the nitrogen in the dry ash-free leather, the amount of pure hide substance may be calculated by the formula—

$$H = \frac{L \times NL}{Nb} ;$$

where H = dry ash-free hide substance.

L = dry ash-free leather substance.

NL = nitrogen in L.

Nb = nitrogen in dry ash-free hide as prepared for tanning, the percent. of N being constant for any one kind of hide.

The difference between H and the pure leather substance gives the amount of combined tannin, which it is important for a practical tanner to know as giving him exact information of the amount and extent of the tannage. This proportion multiplied by 100 may be expressed numerically as the "tanning number" = D :

$$\begin{aligned} D &= \frac{G}{H} \times 100 = \frac{L - H}{H} \times 100 = \left[\frac{L}{H} - 1 \right] 100 \\ &= \left[\frac{Nb}{NL} - 1 \right] 100, \end{aligned}$$

in which G = combined tannin.

From the nitrogen estimation it is possible to calculate how much finished leather 1 part of pure hide substance has yielded. This quantity is expressed in the tables as the "product number" (Rz) :

$$Rz = \frac{100}{H} = \frac{Nb}{L \times NL}.$$

Estimation of Ash.—A weighed quantity of the leather is ignited in a platinum or porcelain dish at a low temperature until the organic matter is completely destroyed. The powdered leather should be added little by little, as it swells considerably when heated. It is important, of course, to prove the absence of the lead before using a platinum dish. The appearance of the ash should be noted, since chromium is easily de-

ected by the colour, and lead and tin may also be looked for by preliminary tests.

Determination of Chromic Oxide.—The ash is fused in a platinum dish or crucible with caustic soda and a little potassium chlorate or nitrate added in order to convert the chromic oxide into chromate. A preferable method, however, is to heat the ash with 3 or 4 grms. of sodium peroxide until it fuses, and keep it in a state of fusion for about 5 minutes. The mass is then allowed to cool partly, another gramme of peroxide is added, and the crucible heated again for 5 minutes. The mass is cooled and extracted with water and the chromic acid estimated volumetrically by the methods already described. The following methods for determination of chromic oxide in leather and its separation from alumina are given by Appelius (*J.S.C.I.*, 1904, 562):—

1. *Determination of Chromic Oxide.*—One to 2 grms. of the leather are incinerated in a platinum dish, 2 to 3 grms. of a mixture of sodium carbonate (60 parts), potassium carbonate (20 parts), and potassium chlorate (4 parts) are added, and the dish heated, at first gently, and finally over a blow-pipe for 20 minutes, a little more of the mixture being added if required. The contents of the dish are then cooled and dissolved in hot water, and the chromic oxide titrated in the usual way with thiosulphate.

2. *Separation of Chromic Oxide and Alumina.*—Two to 5 grms. of leather are incinerated and fused as above. The fused mass is transferred to a porcelain dish with hot water, any barium being filtered off as carbonate, while iron can be determined in the usual way. The clear solution is reduced with alcohol and hydrochloric acid, and any acetic acid formed expelled on the water-bath. The oxides of chromine and aluminium are precipitated with ammonia and weighed, after which they are fused as above and the chromine determined by titration.

Determination of Lead, Barium, etc.—If these have been proved to be present they may be separated from the ash by digesting it with strong sulphuric acid which converts them into sulphates. If the acid be then diluted the sulphates will be thrown down and may be filtered off. When only one of the two is present it may be estimated directly from the weight of the residue. If lead sulphate be ignited it must be done in a porcelain crucible, as it invariably becomes reduced during the process. To ensure against loss the precipitate, before weighing, must be treated with strong acid and again gently ignited. If both lead and barium be present the former may be removed by boiling the mixed residue with ammonium acetate solution containing a little excess of ammonia. It should be boiled with successive quantities of the reagent until the filtrate on allowing to stand gives no coloration with potassium chromate in the presence of acetic acid. The lead is now precipitated as chromate by making strongly acid in acetic acid, adding potassium chromate, and boiling. It is then filtered, dried at 100°, and weighed. The residue will now contain the barium sulphate. If other metals are absent, such as ignited oxides of iron, chromium, etc.,

the residue may be directly weighed. A more accurate method is to fuse it in a platinum crucible with three or four times its volume of fusion mixture, extract with water, acidify with hydrochloric or nitric acid, and precipitate the barium as sulphate. The chromium, iron, and aluminium may also be precipitated from the same solution if present. If lead and barium be absent it is best to fuse the ash at once with fusion mixture, dissolve the fused mass in water, and acidify with hydrochloric acid. As an alternative it may be boiled with strong hydrochloric acid for half an hour; but if chromium, iron, and alumina be present in the leather, it must be remembered that their oxides, when strongly ignited, become practically insoluble in acid. A portion of the acidified solution is made up to 250 c.c. and tested with sulphuretted hydrogen. If group II. metals be absent, 50 to 100 c.c. are treated with ammonia and ammonium chloride, boiled, and filtered. The precipitate is washed into a beaker, boiled with sodium peroxide, and filtered. The residue on the filter paper will consist of iron oxide, the filtrate containing sodium aluminate and chromate. The alumina may be thrown down by means of ammonium chloride while the chromate is titrated. If group II. metals be present 100 c.c. of the solution are precipitated with sulphuretted hydrogen, the precipitate filtered off and the filtrate boiled with nitric acid before adding ammonium chloride, in order to expel H_2S and oxidise the iron salts. A little of the filtrate, after precipitation of the alumina, etc., is tested with ammonium sulphide; if zinc be present, the whole is similarly treated and the mixture allowed to stand on the water-bath for some time, after which the zinc sulphide is filtered off and washed. It is then re-dissolved in dilute acid, precipitated with sodium carbonate, filtered off, washed, dried, and ignited to zinc oxide and weighed. If no zinc be present, the small portion tested is boiled with a little hydrochloric acid to expel sulphuretted hydrogen, made faintly alkaline with ammonia, and returned to the beaker. The contents of the beaker are now boiled and precipitated with ammonium oxalate, as already described. In the almost certain absence of strontium the precipitate will consist of calcium oxalate, which is washed, dried, ignited until constant, and weighed as calcium oxide.

Determination of Titanium.—Since titanium is often much used in tanning, its detection often becomes a matter of importance. When leather is ashed the organic salts of titanium will form a dioxide, which is insoluble in hydrochloric and nitric acid. It may be separated from silica by fusion with potassium hydrogen sulphate and subsequent treatment with water, the titanium forming a soluble sulphate; or it may be separated by fusing with potassium carbonate when potassium titanate insoluble in water is produced. The fused mass is extracted with water, the titanate well washed and boiled with hydrochloric acid, when titanic acid is precipitated. The following confirmatory tests may be applied:—

Ignited TiO_2 is insoluble in water and in most acids: it is easily soluble in HF, less readily in boiling strong H_2SO_4 : it is also rendered

soluble in cold water by fusion with KHSO_4 . TiO_2 differs from SiO_2 by not being volatilised when it is heated in a platinum dish with HF and strong H_2SO_4 .

By *dilution and long boiling*, white flocculent hydrated TiO_2 is precipitated from solution in H_2SO_4 or in HCl, and from the aqueous solution of the fusion with KHSO_4 : the precipitate is meta-titanic acid: it cannot be filtered off unless an acid or AmCl is added.

AmOH , KOH , NaOH , Am_2S , or BaCO_3 , give a white flocculent precipitate, insoluble in excess: if precipitated and washed in the cold, it dissolves in HCl and in dilute H_2SO_4 .

Microcosmic-bead. In the outer flame *yellow* while hot, *colourless* when cold: in the inner flame *yellow* while hot, *violet* when cold.

The production of the above colours is much aided by adding a fragment of Sn. Addition of a small quantity of FeSO_4 causes the bead to become *blood-red* when it is heated in the inner blow-pipe flame.

Determination of Weighting Matter.—Insoluble inorganic substances are sometimes used for this purpose, but the commonest bodies appear to be salts of barium, sugar, and vegetable extracts. Before testing for sugar, tannic and gallic acids must be removed by extracting a weighed portion of the sample with water and precipitating with lead acetate, the excess of lead being removed by sodium carbonate. The sugar in the filtrate is determined by means of Fehling solution or the polarimeter.

Preparation of Fehling Solution.—34.6 grms. of pure re-crystallised copper sulphate are dissolved in water and the solution made up to 500 c.c. One hundred and seventy-three grms. of Rochelle salt and 65 grms. of sodium hydrate are dissolved in water in separate beakers, and the solutions are mixed and made up to 500 c.c. These two solutions are kept in separate bottles, and the Fehling solution made by mixing equal volumes of the two as required.

Determination of Sugar.—(1) *Volumetric Method.*—Ten c.c. of freshly-prepared Fehling solution are placed in a porcelain dish with 40 c.c. of water, and quickly heated to boiling by means of a small bunsen flame. The sugar solution is then run in from a burette in small quantities at a time, boiling for a minute or two after each addition, until the blue colour of the Fehling solution is just discharged. This point may most readily be detected by allowing the precipitate to settle and tilting the dish a little. Ten c.c. of Fehling solution are equivalent to 0.05 gm. of dextrose, hence this number of c.c. run from the burette will contain exactly this quantity of sugar. The drawback to this process is the difficulty of seeing the end reaction. The following method is due to E. F. Harrison (*Pharm. Journ.*, 1903, 170), and renders the end point more delicate:—About 0.05 gm. of starch is boiled with a little distilled water, 10 grms. of potassium iodide added, and the mixture diluted to 100 c.c. About 1 c.c. of this solution is acidified with acetic acid and placed on a porcelain plate in drops. From time to time a

drop of the liquid in the dish is removed with a glass rod and mixed with one of these drops. If copper be present in solution a blue colour is produced, and the titration is continued until no further colour is obtained. The action of the indicator depends upon the fact that copper salts are able to liberate iodine.

(2) *Gravimetric Method.*—Fifty c.c. of freshly-mixed Fehling solution are placed in a beaker of about 250 c.c. capacity and 3 in. diameter. This is placed in a bath of boiling water, and when hot a measured volume of the sugar solution added, and, if necessary, water to bring the total volume up to 100 c.c. The beaker is then covered with a watch-glass and allowed to stand in the bath for 12 minutes, at the end of which time the sugar present will have precipitated its equivalent of cuprous oxide. The latter is collected and washed upon a layer of asbestos pulp in a Gooch crucible previously prepared and weighed. The asbestos for this purpose is prepared by cutting ordinary asbestos into very fine fragments with a pair of scissors and boiling with strong sulphuric acid till the organic matter is destroyed. It is then thoroughly washed and kept in a bottle covered with water. The precipitated cuprous oxide is rapidly filtered through it, washed with hot water, and finally with alcohol and ether, after which it is dried in the water-oven for 15 minutes and weighed. The weight of cuprous oxide multiplied by 0.5042 will give the equivalent of glucose. It is important that the liquid added should be of such a



FIG. 43.



FIG. 44.

volume that the weight of oxide obtained lies between .2 and .4 of a grm. It is also advisable to perform a blank experiment with each lot of Fehling solution, since it sometimes undergoes spontaneous reduction when heated, in which case a correction will be necessary; although it is better in such a case to make a fresh solution. A Fehling solution which undergoes self-reduction may be rendered useful by the addition of caustic soda. Instead of a Gooch crucible the apparatus shown in fig. 43 may be used. It consists of a piece of glass tube

about $\frac{1}{2}$ in. in diameter and 3 in. long, drawn out at its lower end as shown. A useful form is that provided with a stopper for insertion when weighing (fig. 44).

A plug of glass wool is introduced into the narrow end, which is then covered with a layer of asbestos pulp, the tube being then connected with a vacuum pump. It is thoroughly washed with hot water in order to remove any loose fragments of asbestos, dried, and weighed.

In dealing with tanning solutions a difficulty is often introduced by the fact that organic matter is precipitated with cuprous oxide, in which case

it will not be admissible to weigh the cuprous oxide. Under these circumstances the cuprous oxide must either be reduced to metallic copper or oxidised to cupric oxide. To reduce to metallic copper the tube is gently heated in a stream of dry hydrogen gas, great care being taken not to fuse the glass wool. After the reduction is complete the tube is dried again and weighed. If the precipitate be weighed as cupric oxide it is only necessary to ignite it in the presence of air until the weight is constant, but in this case a good crucible should be employed. The following are the factors for the transformation of copper and its oxides into sugar:—

	Glucose.	Cane-sugar after inversion.
Cu,	·5634	·5395
Cu ₂ O,	·5045	·4790
CuO,	·4535	·4308

Estimation of Cuprous Oxide by Titration with Permanganate.—When cuprous oxide is uncontaminated by organic matter the simplest and quickest method of estimation is that of Caven and Hill (*J.S.C.I.*, 1897, 981).

The following solutions are required:—

1. Fifth normal potassium permanganate solution of which the oxygen value is known.
2. An oxalic acid solution of the same strength as the permanganate.
3. Dilute sulphuric acid containing 1 part of acid to 3 of water.

A filter mat of asbestos pulp is prepared as described above, using either a Gooch crucible or a filter funnel with a perforated plate. As soon as the precipitation of the cuprous oxide is complete the supernatant liquid is decanted through the filter, the oxide washed with hot water, transferred to the filter, and washed till free from alkali. It is not of importance to remove at this stage every trace of cuprous oxide from the beaker. The asbestos, together with the cuprous oxide, is now transferred to a porcelain dish and thoroughly broken up with water. If the quantity of oxide is not more than .2 gm., 25 c.c. of the standard permanganate are mixed with 100 c.c. of the dilute sulphuric acid in the beaker containing the residual traces of cuprous oxide, and after standing for a few minutes poured into a dish. Boiling water is now added until the temperature is about 50° C. and the mass well stirred, the beaker being carefully rinsed out at the same time into the dish. After a few minutes the cuprous oxide will have dissolved and become oxidised at the expense of the permanganate. The excess of permanganate is now titrated with the oxalic acid solution. From the volume of permanganate used the equivalent of cuprous oxide is obtained by multiplying the oxygen value by the factor 8·91, and the cuprous oxide converted into dextrose by multiplying by 0·5042.

Mineral Weighting Matters.—These will have already been identified in the analysis of the ash.

Specific Gravity.—The relative weight (density) of a given volume (100 c.c.) of leather—determined by weighing a number of discs of known dimensions, cut from the sample—affords a good indication of the quality, and should exceed 124 (grms.). Weights between 121 and 123 are admissible, but indicate incomplete tanning, and leathers prepared by the quick method of tanning do not greatly exceed 110 grms., whilst really bad grades weigh 85–87 grms. Loaded leathers are open in texture, and exhibit a high co-efficient of absorption of moisture per unit of time (weight of H₂O absorbed in 1 hour divided by weight of extractive matter), and this co-efficient varies inversely with the density of the leather, e.g. 0·000174 for a sample weighing 130·7 grms. per 100 c.c. and 0·000384 for another weighing 87·6 grms. By dividing the co-efficient of absorption multiplied by 1,000,000 by the density, direct values for quality can be obtained, the results being, 1·33 (best leather) and 4·38 for a leather of inferior grade.¹

Rowland A. Earp (*Collegium*, 1906, 422) gives the following method:—

To determine the “apparent” specific gravity, which is that of the leather with its included air and moisture, a piece is taken 2 or 3 grms. in weight and about 7 cms. long. A stout glass-stoppered bottle with a wide curved-in rim and a stopper about 1·5 cm. in diameter is filled with mercury and the stopper screwed in till it is tight; the excess of mercury which gathers round the rim is poured off, the stopper removed, and the leather inserted endways, being pushed down with the stopper until the latter is tight. The mercury now in the rim is that displaced by the leather, and measures its volume, which is determined by weighing the mercury. If w be the weight of the leather, m the weight of mercury, then sp. gr. = $w \frac{m}{13\cdot56}$.

To determine the “real” specific gravity or that of the actual leather substance, 2 or 3 grms. of it are dried until of constant weight. A tube graduated to tenths of a c.c. is partly filled with common lamp petroleum and clamped vertically with a mirror behind. The meniscus, top and bottom, is read, and the mean taken as the level. The leather, dried and weighed, is dropped in and left until no more bubbles escape, showing that the petroleum has soaked the leather and expelled all included air. The volume is then read, and the difference in the readings gives the volume of the leather substance. This divided into its weight is the specific gravity. Both methods are said to be accurate to ·2 per cent.

The second method has the disadvantage that the paraffin permeates very slowly and that single determinations only can be made. The following modification (*loc. cit.*):—Samples of the perfectly dry leather (2 to 3 grms.) are immersed in a bottle of paraffin of known specific gravity. They are left for a night, taken out, wiped, and weighed. Their volumes are then determined by the mercury method.

¹ *Bull. Assoc. Belge des Chim.*, [4], xiii, 189–194.

The three data—original weight, final weight, and the volume—are enough for specific gravity determination.

Let W = original weight.
 w = increase in weight.
 S = specific gravity of leather.
 s = specific gravity of oil.
 V = volume of leather as determined.

Then if v_1 and v_2 be the volumes of the leather substance and the oil absorbed respectively, we have—

$$\begin{array}{rcl} v_1 + v_2 = V, & . & 1 \\ Sv_1 = W, & . & 2 \\ sv_2 = w, & . & 3 \end{array}$$

Substituting for v_1 and v_2 in (1)—

$$\frac{W}{S} + \frac{w}{s} = V;$$

i. e. $S = \frac{Ws}{Vs - w}$.

Example.—The specific gravity s of the paraffin was found to be 0.8245. Original weight, $W = 1.947$ grms. Final weight, $W + w = 2.398$ grms., or $w = 0.451$ gm. Volume of mercury displaced = 1.859 c.c.

$$\text{Thus } S = \frac{1.947 \times 0.8245}{1.859 \times 0.8245 - 0.451} = 1.484 \text{ grms. per c.c.}$$

Determination of Mineral Acids.—This determination is often of considerable importance and various methods have been proposed, but there is some difficulty in obtaining absolutely accurate results. Since mineral acids are soluble in alcohol to the exclusion of the neutral salts, the simplest method would be to extract thoroughly with alcohol and estimate the acid in the extract, but it is found in practice that it is almost impossible to extract the whole of the acid in this way. A similar objection applies to another method sometimes used, namely, that of boiling the leather with alcohol. A modification of this method has, however, been proposed by Procter and Searle (*J.S.C.I.*, 1901, 287). A quantity of leather weighing about 3 grms. is finely shredded and placed in a platinum dish, with a measured quantity of decinormal sodium carbonate. About 20 c.c. is generally sufficient. It is then evaporated to dryness on the water-bath and ashed at a low temperature until the organic matter has been entirely burnt. Thirty c.c. of decinormal hydrochloric acid are then added and the dish warmed to aid solution. The liquid is then filtered, the filter being thoroughly washed, and the filtrate is titrated with decinormal sodium carbonate and methyl orange. The total volume of decinormal alkali used *minus* that of the acid gives the amount of mineral acid present, and its nature having been ascertained by previous qualitative tests, its quantity can be calculated. The following method depends upon the insolubility of benzidine sulphate,¹

¹ This compound does not, however, appear to be quite insoluble.

and was proposed by M. C. and J. W. Lamb. The description of the process is taken from the *Journal of Society of Chemical Industry*, 1904, 134):—

(a) *Total Free and Combined Acid*.—Five grms. of the shredded leather are dissolved in a flask on the water-bath in pure caustic soda solution (25 c.c. of 10 per cent. strength), with sufficient water to cover the material. The liquid is then made acid to phenolphthalein with strong hydrochloric acid (20–25 c.c.), filtered, and, with the washings, evaporated to dryness in a platinum dish. The residue is ignited, dissolved in a little weak hydrochloric acid (30 c.c. of normal solution), diluted, filtered (if necessary), the filtrate treated with 200 c.c. of benzidine hydrochloric solution, and the mixture allowed to stand for 15–20 minutes. It is then filtered with the pump on a porcelain disc, and covered with two well-fitting papers, the flask being rinsed out by means of the filtrate, which should also be tested for complete precipitation. The precipitate is washed twice with 10 c.c. of water (the last washing should be neutral to litmus), transferred together with the filter paper to a flask, and there broken up with 50 c.c. of water by violent agitation in the corked flask.

The contents are now titrated with $\frac{N}{10}$ caustic soda solution, using phenolphthalein as indicator, and when apparently just alkaline heated to 50°–60° C.; the faint alkalinity is restored by further titration, and again, after boiling, the total volume (a) of $\frac{N}{10}$ alkali being recorded.

(b) *Combined Acid only*.—Another portion of the leather (5 grms.) is gently coked in a platinum dish, the carbon is burnt off in a stream of oxygen gas at a minimum temperature to avoid loss of sulphates, and the residual ash is strongly ignited over the blowpipe for 5 minutes. It is then dissolved in weak hydrochloric acid, the solution filtered, and the sulphuric acid determined as in a . If b = the number of c.c. of $\frac{N}{10}$ caustic soda solution required, then $(a - b) \times 0.0049$ gives the amount of free sulphuric acid in the leather.

Preparation of Benzidine Hydrochloride.—Commercial benzidine (12.5 grms.) is ground up in a mortar with 50 c.c. of water, transferred with hot water to a litre flask, and, after addition of strong hydrochloric acid (15 c.c.), made up to the mark. This solution is filtered and diluted to 5 litres for use as a reagent, of which 100 c.c. precipitates about 0.1 gm. of sulphuric acid, representing 2 per cent. of acid in 5 grms. of leather.

Other Methods.—L. Meunier (*Collegium*, 1906, pp. 15, 296) thinks the incineration method is unsuitable for an official one for the determination of sulphuric acid in leather, since a variable portion of the sulphur is not retained by the alkali during incineration. The following modification of the method of Nihoul and Konnick gives good results:—

A hard glass tube about 50 cm. in length is bent and drawn out at one end. A plug of glass wool is placed near the bend, upon it about 20 cm. of pure granulated calcium nitrate, and then a mixture of small fragments of the leather and calcium nitrate. A current of oxygen is led through the open end of the tube, and the bent delivery tube dips beneath the surface of an alkaline solution. The portion of the tube containing calcium nitrate is now carefully heated, and subsequently the heating extended to that portion containing the leather and nitrate. The leather burns easily in the presence of oxygen, and any volatile products escaping primary combustion are burnt up by the calcium nitrate, and the sulphuric acid formed is retained by the lime. When combustion is complete the receiver containing the alkali is removed, and the contents evaporated to dryness in a platinum dish and incinerated over a spirit lamp. The residue is dissolved in hydrochloric acid and tested for sulphates. If the experiment has been properly carried out these should be absent. When cool, the contents of the tube are transferred to a beaker with water, and nitric acid neutralised if present. Hydrochloric acid is then added, and sulphuric acid is determined in the usual way.

The process is accurate, but somewhat long and difficult on account of the large quantity of saline matter in the solution.

In the following method these difficulties are obviated:—The leather is burnt in oxygen in a Mahler's bomb calorimeter under a pressure of 30 atmospheres in the presence of a known quantity of soda, and the sample is then placed in the platinum capsule and the bomb closed. The combustion is carried out in the usual way. When complete the contents of the bomb and capsule are washed out, mixed, if necessary, filtered, acidified with hydrochloric acid and evaporated to dryness in a porcelain dish. The residue is moistened with strong hydrochloric acid and re-dried once or twice to expel nitric acid formed during the combustion. It is then dissolved in dilute acid and the sulphuric acid precipitated with baryta.

If A be the percentage of SO_3 calculated on the dry leather and B the percentage present in the ash as neutral sulphate, and C the percentage corresponding to the average sulphuric content of the skin substance of leather, then $X = A - (B + C)$ where X is the percentage of SO_3 corresponding to the free acid of the leather. C must be experimentally determined once and for all.

The last two methods, while suitable for leather tanned with vegetable tannages, are inadmissible in the case of chrome leathers containing free sulphur, since this will also be oxidised to sulphuric acid during the combustion.

Sulphur.—Chrome leathers made by the two-bath process will always contain free sulphur. A portion of this may be extracted with carbon bisulphide, but part of it is always insoluble in this solvent. To determine free sulphur the following process should be adopted:—

Boil the finely shredded leather with moderately concentrated hydrochloric acid till it is completely disintegrated and the skin substance and chrome dissolved. Filter off the insoluble residue, which will contain all the free sulphur, and oxidise it with fuming nitric acid till all the sulphur has been oxidised. Then dilute, and estimate the sulphuric acid by precipitation with barium chloride.

If total sulphur be required the original leather can be directly oxidised with fuming nitric acid.

CHAPTER XVIII.

FLESHINGS AND SCUTCH.

GREAT care must be taken before analysing these bodies to obtain a representative sample, and it is best to pass a good deal of the sample through a mincing machine. Having obtained a fair sample, the following determinations should be made:—

Moisture.		Fat.
Mineral Matter.		Gelatin.

The determination of moisture, ash, and fat will, of course, present no difficulties, being done in the usual way.

Gelatin may be determined by boiling about 20 grms. of the substance with water until it is thoroughly extracted, filtering, washing, and treating the filtrate with excess of tannic acid in the presence of salt and sulphuric acid. This will throw down all the gelatine, together with any peptones that are present. The precipitate is filtered and the nitrogen content determined. For this purpose the filter-paper, together with the precipitate, is placed in a Kjeldahl flask with about 20 c.c. of acid. The nitrogen is estimated as gelatin by means of the usual factor. This method will, of course, co-estimate any traces of peptone that may be present. If it is desired to separate the gelatin from the peptone the solution must be saturated with zinc sulphate, which will throw down the gelatin and leave the peptone. The precipitate is filtered off and treated as before. It may sometimes be necessary to determine phosphoric acid in scutch. The method has already been described in connection with *Bates*.

Fat is determined by drying a weighed portion of the sample or sand, powdering and extracting the dried mass with petroleum in a Soxhlet extractor. Since, however, a large portion of the fat will be present as lime soap, it is necessary, in order to obtain the total fatty matter, to previously heat with hydrochloric acid. The process may be simplified by pouring the decomposed mass into a graduated cylinder, diluting with water and shaking with petroleum. After this has separated its volume is read and an aliquot part propelled off and evaporated to dryness.

CHAPTER XIX

GLUE.

THE best glues and many gelatins are made from skin waste. The process, in brief, consists in boiling and removing the fat, then clarifying by filtration or precipitation, casting into blocks and drying. A skin glue may be distinguished from a bone glue by the absence of chondrin.

A good glue should be clear when viewed by transmitted light and neutral or faintly acid in reaction, and its aqueous solution should not possess an unpleasant smell. It should, when placed in water for 48 hours, absorb about five times its weight, forming a clear firm jelly. It is dissolved by acids and alkalis with the formation of gelatones (hydrolysed gelatin) and peptones. The ash should not be much more than 2 per cent. In a bone glue this will consist chiefly of lime and phosphate; while skin glues often give an ash containing soda, in which case they are fusible.

The analysis of glue has been the subject of much work and discussion, so that finality has not yet been reached. This is owing to the fact that gelatin is an extremely complex compound, about which little is really known, the changes which it undergoes during hydrolysis and other forms of degradation being still less understood. Hence a good many of the methods proposed for its analysis are empirical and unreliable, since an empirical method can never take account of varying conditions.

The tests that are applied are broadly divided into two classes—viz., chemical and physical.

The physical tests are much favoured by the trade and are almost innumerable. They are, however, not in the slightest degree comparable one with another, and depend entirely upon the personal factor. Of course, they are valuable and intelligible to the man who makes them, but usually to no one else. Physical tests, moreover, have the grave defect that although they may distinguish between a good glue and a bad one, they are quite incapable of pointing out the cause of the difference as a chemical analysis should do. In fact, while they serve a useful purpose for sorting glues or for a buyer, they are of little value from a manufacturing point of view.

The following are the more important of the physical tests that have been proposed:—

- (1) Melting point of jelly.
- (2) Water absorbed.
- (3) Strength of jelly.
- (4) Breaking strength of joint made with the glue.
- (5) Viscosity.
- (6) Foaming capacity.

• **Melting Point of Jelly.**—Fifteen grms. of glue are soaked overnight in 30 c.c. of water, dissolved by warming, and poured into a test-tube; this is corked and cooled to 15° C. The tube is then laid in a horizontal position in a metal bath, surrounded by a water jacket, and carefully heated till the horizontal section of the glue begins to incline, the temperature at which this occurs being the melting point. The temperature is measured by means of a thermometer inserted in a second tube, filled to a similar height as the first with a solution of gelatin containing 1 part of gelatin to 1 of water.

Wenkilblech's method (*Z. angew. Chem.*, 1906, 19, 1260; and *J.S.C.I.*, 1906, p. 769) depends upon the determination of the temperature of gelatinisation of an 8 per cent. solution. The glue is soaked overnight in cold water and then dissolved in water at 40° to 50° C., and the solution made up to 500 c.c. at 40° C. About 400 c.c. of this solution are placed in a flask fitted with a cork, through which passes a thermometer in such a way that the bulb is in the middle of the flask. The flask is then cooled with continual shaking till gelatinisation occurs. The following are some comparative results with solutions of glue containing 80 grms. per litre:—

TABLE LVI.

Gelatin,	20·0° C.
Joiners' glue,	11·0
Cologne I.,	11·0
Cologne II.,	8·7
Mulbouse,	7·0
Russian,	4·0

Water Absorbed.—A weighed quantity (5 grms.) of the glue is placed in a beaker or suspended with a fine silk thread and covered with cold distilled water for 48 hours. The water is then wiped off and the glue weighed and its appearance noted. Good glues will absorb at least five times their weight of water when treated in this way, and the jelly formed will be clear and firm and devoid of smell.

The time of soaking may be with advantage shortened to 24 hours, in which time about three times the weight will be absorbed by a good glue.

Strength of Jelly.—An almost endless number of tests have been proposed for this purpose. The following are some of the better known:—

Lipowitz Method.—A 10 per cent. solution of the glue is allowed to

set in a glass cylinder. A small cylindrical metal cup is then placed on the surface of the glue. To this cup is fastened a vertical metal rod, which passes through a support at the top of the cylinder to keep the apparatus vertical in position. At the top of this rod is a second cup, which is loaded with shot until the lower one sinks to a certain point in the jelly, the weight of the shot used being recorded. A simplification of this method is suggested by Rideal (*Glue and Glue Testing*, p. 121), who places a small tube or beaker on the surface of the jelly and loads it until it sinks. He finds that a 10 per cent. jelly will bear a weight of from 12 to 64 grms., falling to zero in the case of bad glues.

Kissling's Test.—A series of pointed rods made of glass, zinc, and brass, and weighing 50, 100, 150 grms., are provided with a cap at the upper end; a guide is made use of, as shown in fig. 44A,¹ the distance between the cap and support being 100 mm. The diameter of the rods is from 8 to 10 mm.

A jelly is made by soaking 100 grms. of the glue in 300 c.c. of water for some hours, then dissolving by means of heat, and afterwards allowing it to set to a jelly. The point of the rod is then placed upon the jelly and the time taken to sink till the cap rests upon the guide measured.

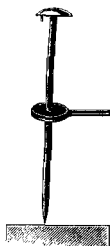


FIG. 44A.

Kissling (Rideal, *Glue and Glue Testing*, 121) gives certain arbitrary standards for glues. If the rod takes 850 seconds or longer to sink, the consistency is 100, while if the glass rod sinks in one second the consistency is zero. The results obtained by this and the shot test do not agree, owing to the fact that in the

latter the skin offers a considerable resistance to the cup. By cutting off this skin more comparable results are obtained. According to Rideal the difficulty may be overcome by allowing the solutions to set in cylinders with false bottoms. These are completely filled with the liquid, and, when tested, inverted, and the false bottom removed. The jelly will bear a considerable weight without actually breaking, recovering itself when the weight is removed. The point to be observed is when the meniscus formed by the sinker suddenly rises, showing that penetration of the surface has taken place. The same author recommends the use of a test-tube as a sinker which is weighted with shot or mercury, while the vessel containing the jelly is graduated in millimetres. The tube will penetrate the jelly to a certain depth, depending on its weight, and then stop. By adjusting the weight in the test-tube it can be made to stop when the end is 100 mm. from the surface of the jelly. The consistency is measured in terms of the weight required. The positions of equilibrium are due to—

1. The resistance becoming greater as the tube sinks deeper into the jelly.
2. The displacement of the gelatin in the cylinder.

¹ Rideal, *Glue and Glue Testing*, p. 120.

As the result of experiment Rideal recommends the following method of procedure:—First note the weight required to break the surface. The weight of the tube is, of course, constant, and shot or mercury is added till the surface is first broken, the weight added being determined by difference. Then take another cylinder of the jelly and place the weight found in the above experiment immediately on the jelly and measure the time it takes to traverse the required distance.

Reliable results have been obtained in the author's laboratory with a siphner of the shape shown in fig. 45, where $CD = \frac{1}{2}$ inch and AB 9 inches. Weights are gradually placed in the upper cup till the surface is broken.

Finger Test.—This method has been found by the author to give far better results than any other physical test tried.

Ten grms. of the glue are dissolved in 100 c.c. of water and allowed to set in a cylindrical pot. In a number of exactly similar pots varying weights of a standard glue or gelatin (Coignet's gold label) are dissolved in 100 c.c. of water and allowed to set side by side with the glue. When these have all set the strength of the glue jelly is matched against them by lightly pressing the surface with the finger tips, and that particular strength of gelatin noted which offers the same resistance to the finger as the glue. The strength of the jelly is then expressed as a percentage of the standard used. For instance, 10 grms. of glue gave a jelly equal in consistency to that obtained from 3.5 grms. gelatin. Hence the consistency of the glue is said to be 35.

Breaking Strain of Joints.—An immense number of tests of this description have been proposed, but they are of little use, duplicates never agreeing, doubtless owing to the difficulty of making the joint in exactly the same way twice following. The author has made a large number of experiments with blocks of wood which were glued together and the breaking strength measured in a machine with a recording dial, but with unsatisfactory results. The results are influenced by so many factors that any test of this description is liable to give highly erroneous results. The same remarks, of course, apply to the cabinetmaker's test of glueing two pieces of wood together and breaking the joint across the piece. Rideal uses hard but moderately porous blocks of biscuit stoneware. These are glued together and allowed to set for five days. They are then placed in a specially-made machine consisting of a system of levers, and a tub into which shot or sand is poured till the joint breaks, the quantity necessary being afterwards weighed.

Viscosity.—Much reliance is often placed on this test, but it must be remembered that it measures adhesiveness, a property quite distinct



FIG. 45.

from consistency. Thus a liquid glue may have a high viscosity but be unable to form a jelly. In reality viscosity is misleading, since it only measures quantity and not quality.

Engler's viscometer is largely used for glues, but the instrument possesses no advantage over any form of burette viscometer, and the results obtained are quite arbitrary. Engler uses a 15 per cent. solution at 30° C. and measures the time of experiment for 500 c.c., comparing it with the time taken by an equal volume of water under the same conditions.

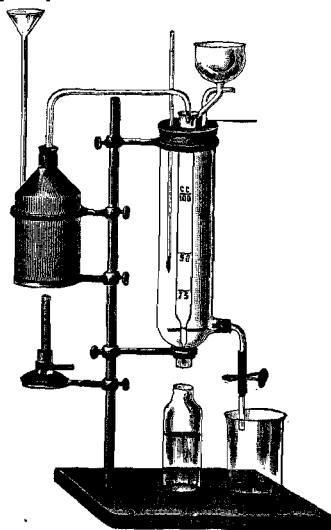


FIG. 46.—Archbutt's Viscometer.

Equally reliable results may be obtained with much cheaper forms of apparatus, and of these Archbutt's viscometer answers admirably. It also has the advantage that the absolute viscosity may be readily deduced if the apparatus has previously been standardised with solutions of glycerine of known strength.

Description of Archbutt's Viscometer (fig. 46).—A stout glass burette with a short stem is graduated to 25, 50, and 75 c.c., reckoning from a zero mark placed a little below where the jet begins. It is surrounded by a water-jacket ending at the bottom in a neck closed by a thin rubber cork

pierced for the stem of the burette. The jacket is closed at the top by a large rubber bung, with holes to admit the burette, a funnel tube for pouring in water, thermometer, stirrer, and tubes for the entrance and escape of steam. Near the bottom of the jacket is a side aperture for running out water.

The clean dry burette is pushed through the large bung until its stem projects about $\frac{3}{16}$ in. below the cork, but not beyond the glass neck. So adjusted, chilling of the glue during its outflow is reduced to a minimum. For ordinary glues a 15 per cent. solution at 30° C. is convenient for viscosity determinations. The jacket is filled with water at that temperature, the jet of the burette plugged with a peg of soft wood, and the glue solution, previously heated to 30° C., poured into the burette to a point above the 50 c.c. mark. When the glue is exactly at 30° C., determined by stirring with a thermometer, the peg is withdrawn from the jet and the glue allowed to run out. A stop-watch is started the moment the surface of the glue solution reaches the 50 c.c. mark and stopped the moment it passes the zero mark, the time taken being compared with that taken by standard glue, water, or an oil of known absolute viscosity measured by the same instrument.

For further details, Archbutt and Deeley's *Lubrication and Lubricants* may be consulted.

Foaming.—However good a glue may be, it may be quite spoiled for many purposes by its tendency to foam. Foaming is tested in various ways, but unless similar conditions are observed the results of two experimenters will not agree. The commonest form of test is to make a 10 per cent. solution, shake it in a stoppered cylinder, and read off the height of the foam. Since the foam is dependent on—

- (1) The height of the liquid in the tube,
- (2) The diameter of the tube,
- (3) The temperature of the solution,

it is evident that a standard method of testing is of importance. The following method has been proposed by Trotman and Hackford (*J.S.C.I.*, 1906, p. 105):—

A graduated tube, about 70 cm. in length, and of such diameter that each division is 1 cm. in length and has a capacity of 1 c.c., is half filled with a solution of the glue to be tested and placed in the water-jacket, the temperature of which may be raised by passing steam into it. The even distribution of the steam is effected by means of a ring at the end of the delivery tube, and an overflow is provided. The temperature of the bath is maintained at 60° C., which is a convenient one for glue solutions. After allowing sufficient time for the temperature of the glue solution to reach 60° C., the tube is withdrawn from the bath and its level adjusted by means of the tap till it stands at zero, there being then exactly 25 c.c. of the solution in the tube. The tube is now corked and shaken vigorously

for about a minute, replaced in the bath, and the height of the foam read off. The top of the foam is read, since this is found to be constant with a constant temperature. The line of demarcation between the foam and the liquid is too indistinct to allow of the lower reading being accurately taken. The higher reading is so constant that different operators can always obtain the same figures. Since the foam produced always varies with the temperature, the importance of carrying out the test at a constant temperature is apparent. Measured in this way the foam figure for a good glue is about 10.

Colour.—This may be measured, if necessary, by means of the Lovibond tintometer or by dilution in a graduated cylinder against a standard.

Chemical Analysis of Glue.—*Moisture.*—About 5 grms. of finely powdered glue are weighed in a flat dish and dried in the oven until constant in weight. A good glue will usually contain from 14 to 16 per cent. of water. Excess of water not only means deficiency in glue, but will aid putrefaction, while, on the other hand, over-dried glues are often deficient in adhesive power.

Ash.—The dry residue is incinerated at a low temperature and weighed. The reaction of the ash and its composition should be noted, and it should be tested for boric acid.

Acidity may consist of fixed and volatile acids. The total acidity is determined by diluting 10 c.c. of a 10 per cent. solution of the glue and titrating with decinormal soda and phenolphthalein. A second quantity of 10 c.c. is then diluted, boiled down once or twice to expel volatile acids, and the residual fixed acid titrated again. The volatile acid is calculated as acetic and the fixed as lactic acid.

Mineral Acids.—For some purposes mineral acids or sulphur dioxide are very objectionable in glue. Free sulphurous acid may be detected and estimated by distilling the glue with steam and titrating the distillate with decinormal iodine solution and starch, afterwards testing the solution for sulphates, and, if necessary, estimating them as a check. Free sulphuric and hydrochloric acid may be determined by one of the methods given for leather, remembering that no glue which gives an alkaline ash can contain free mineral acids.

Fat.—Five grms. of dried glue are extracted in a Soxhlet apparatus with petroleum ether for about four hours. Only traces of fat should be present. Any perceptible quantity renders the glue turbid and spoils its adhesive properties. The above method makes no allowance for soaps. If these are present the glue is boiled with hydrochloric acid and dried on sand. It is then powdered and extracted in a Soxhlet apparatus with petrol.

Non-Gelatinous Bodies.—According to Clayton (*J.S.C.I.*, 1902, 670) this determination is the best single test for the valuation of glue. Stelling's process (*Analyst*, 1896, 239) is as follows:—

Fifteen grms. of glue are soaked over-night in 60 c.c. of water in a

250 c.c. flask. Next day the jelly is dissolved on the water-bath and the loss by evaporation made up. The flask is then filled with 96 per cent. spirit¹ and thoroughly shaken. After standing 6 hours, 25 to 50 c.c. are filtered off and evaporated, the residue containing the non-gelatinous bodies dried at 100° C. and weighed. The following results were obtained by Stelling:—

TABLE LVII.

Glues,	from 2.0 - 4.70	mean 3.49
Leather glues,	„ 4.30 - 7.60	„ 5.73
Bone glues from acid bones,	„ 9.24 - 11.84	„ 10.33
Bone glue from neutral bone,	„ 14.30 - 32.10	„ 20.66

Nitrogenous Constituents.—Several methods are in use for the determination of the nitrogenous constituents, the commonest being the estimation of total nitrogen and its calculation to gelatin. Other methods depend on the power which tannic acid has of precipitating gelatin. Nearly all these methods are open to the grave objection that they either precipitate or co-estimate peptones with gelatin.

Determination of Gelatin by Kjeldahl's Method from Nitrogen Content.

—The weak point of this process is that it fails to distinguish between gelatin and other nitrogenous bodies present. If glue be over-boiled, it undergoes chemical change resulting in a decreased power of adhesion, but there is no alteration in the nitrogen content from which, in this method, the percentage of gelatin is calculated.

About half a gram. of powdered glue is employed for the experiment. The factor for converting nitrogen values into gelatin values is 5.56.

Determination of Gelatin by Precipitation with Excess of Tannin.

—A weighed quantity of the glue under examination (about 5 grm.) is dissolved in water, acidified with dilute acetic acid and a solution of tannin added till present in distinct excess. The precipitate is allowed to settle, washed, as far as possible, by decantation, and finally transferred to a filter and dried. The filter and its contents are now transferred to a Jena flask and the nitrogen determined by the Kjeldahl method as before.

The above method has been made volumetric by Williams by an application of Löwenthal's process for the estimation of tannin¹(*q.v.*). For this purpose a weighed quantity of glue is dissolved in sufficient water to make a 1 per cent. solution, and to this is added a known excess of standard tannic acid solution together with the usual quantity of salt solution, the precipitated gelatin filtered off and the excess of tannin titrated with the standard permanganate and indigo-carmin solutions. The gelatin present is calculated on the assumption that 42.7 parts require 57.3 of tannin for precipitation, but it has been shown that the composition of the precipitate is not constant.

Another variation of this process is described by F. Jean (*Analyst*,

¹ Gelatin is insoluble in spirit of this strength.

1897, p. 164). One gram. of gelatin is dissolved in 100 c.c. of water; 10 c.c. of this solution are mixed with an equal volume of a 1 per cent. solution of pure tannin, and the mixture agitated with 5 grms. of sodium chloride and 1 gm. of acid sodium carbonate, to render the gelatin tannate insoluble. After passing through a quick filter the liquid is collected in a glass graduated at 45 and 60 c.c., the first-named volume being made up by washing the precipitate with a solution of sodium chloride of specific gravity 1.184. A solution of iodine (4 grms. per litre) is now added drop by drop until the presence of free iodine is shown by starch. The liquid is made up to the second mark with distilled water, and the addition of iodine continued until a faint blue coloration is observed. From the volume of iodine used the excess of tannin is calculated, the difference between this and the original quantity of tannin taken being that required for the precipitation of the gelatin. The tannin solution is freshly made and standardised for each set of experiments.

Determination of Gelatin by Means of Chlorine or Bromine.—This process is based on the fact that chlorine or bromine precipitates gelatin in a granular form, which can be readily weighed. It was first suggested by Rideal and Stewart (*Analyst*, 1897, p. 228), who pass a rapid stream of chlorine through a solution containing not more than 0.2 per cent. of proteids until a granular precipitate is obtained and the supernatant liquid contains excess of chlorine. The precipitate is then filtered on a hard filter, washed till free from chlorine, drained as dry as possible, then dried in vacuo and weighed. According to Rideal and Stewart the weight of this precipitate multiplied by 0.78 gives the quantity of proteid present.

This process has also been examined by Allan and Searle (*Analyst*, 1897, p. 258), who find that by substituting bromine for chlorine the time required for the determination may be lessened without impairing the accuracy of the process. They recommend the following mode of procedure:—

“A quantity of the solution containing about 1 gm. of the albuminoid matter is brought to a volume of about 100 c.c. and treated in a conical beaker with sufficient dilute hydrochloric acid to render the liquid distinctly acid to litmus. Bromine water is then added in considerable excess, and the liquid stirred vigorously for some time.” A yellowish precipitate is formed, at first flocculent, but becoming viscous and adhering to the sides of the beaker on stirring. The beaker is allowed to stand till the precipitate has settled, when the liquid is decanted through an asbestos filter made by placing a little glass wool in a cylindrical funnel and covering it with a pad of pulped asbestos. The precipitate adhering to the sides of the beaker is washed several times with cold water, the washings being poured through the filter. It is advisable to keep the washings separate from the filtrate and wash with sodium sulphate solution

of bromine water, since sometimes, when most of the free bromine has been washed out of the precipitate, the liquid does not filter clear.

After the completion of the washing the filter plug and precipitate are returned to the beaker in which the precipitation took place, 20 c.c. of strong sulphuric acid added, the beaker covered with a watch-glass and heated on a wire gauze. When frothing has ceased 10 grms. of powdered potassium sulphate are added and the heating continued till a colourless solution is obtained, when the nitrogen is estimated in the ordinary way by the Kjeldahl method.

Estimation of Gelatin by Difference.—If the non-gelatinous bodies have been determined by Stelling's process (as described above) the gelatin may be determined by difference. This, however, is rarely done, although Stelling, supported by Clayton, considers that the determination of the non-gelatinous bodies is an extremely valuable test.

Precipitation of Gelatin with Zinc Sulphate.—All the above tests are open to the objection that they make no attempt to differentiate between the different forms in which nitrogen is present, but assume that in all it is of equal value as glue.

This is, however, by no means the case, variable quantities of peptone and other nitrogenous bodies being nearly always present, depending in amount on the process of manufacture and the value of original raw materials. It has been shown (Trotman and Hackford, *J.S.C.I.*, 1906, 104) that peptones exercise a very deleterious effect on glue, causing a great increase in the foam and a decrease in consistency when present to any considerable extent, as shown by Table LVIII.

TABLE LVIII.

No.	Amount of Gelatin.	Amount of Peptones.	Relative Consistency.
1	100	0	400
2	"	$\frac{1}{2}$	420
3	"	1	420
4	"	2	430
5	"	3	453
6	"	4	570
7	"	5	475
8	"	10	415
9	"	20	367
10	"	30	345
11	"	40	290
12	"	50	240
13	"	60	166
14	"	70	154
15	"	80	132
16	"	90	125
17	"	100	96
18	"	100	0

In these experiments the quantity of gelatin present was kept constant,

and hence the deleterious effect of peptones on the consistency is not so well seen. Where peptones replace gelatin, as in manufactured products, a rapid fall in consistency is observed, as seen in Table LIX.

It sometimes happens that nitrogenous bodies of a lower grade and of less value than peptones are also present, hence it is obvious that no method of analysis can be really satisfactory which does not take some account of these different combinations. To meet this difficulty Trotman and Hackford (*J.S.C.I.*, 1904, 1072) have proposed to utilise the facts that gelatin is precipitated by saturating its solution with magnesium or zinc sulphate, while peptones remain in solution. The latter can be determined in the filtrate by precipitation with bromine (as described above). After precipitation by bromine the filtrate may be Kjeldahl'd for the determination of amides, etc., and thus the total nitrogen divided into three portions, viz. :—

1. True gelatin.
2. Peptones or hydrolysed gelatin.
3. Lower nitrogenous compounds.

That the value of a glue as measured by its consistency closely follows the zinc sulphate figure is shown by Table LIX.

TABLE LIX.

	Consistency.	Total N \times 5.56 by Kjeldahl.	N pptd. by $\text{ZnSO}_4 \times 5.56$ = Albumoses.	Peptones by Difference.
1	150	74.03	72.22	1.81
2	140	74.03	71.36	2.67
3	135	71.64	69.54	2.10
4	120	74.62	68.05	6.57
5	110	74.30	67.0	7.30
6	90	71.04	64.18	7.86
7	40	73.02	57.99	15.03

An inspection of this table will show that the total nitrogen determination alone is of very little value.

The method used is as follows :—

One gm. of finely powdered glue, or its approximate equivalent of size, is dissolved in a quantity of water not exceeding 20 c.c. While still hot, zinc sulphate crystals are added in excess to saturate the solution. It is then well stirred by a rod or mechanical stirrer, filtered through a funnel containing a plug of glass wool forced into the stem, and washed with saturated zinc sulphate solution. The glass wool and precipitate are subjected to analysis by Kjeldahl's method, the nitrogen found multiplied by 5.56 giving the albumoses present.

Alternative Method.—The solution is made of the same strength as before. Zinc sulphate crystals are used in considerable excess, so that the

solution becomes viscid. It is then stirred in a small beaker or tube with a rod—keeping the solution hot—whereupon the albumoses cling to the rod and to the sides of the vessel, leaving the solution practically clear. If the precipitated albumose still float after stirring, the addition of more zinc sulphate will cause it to coagulate and stick to the rod. The remaining liquid is decanted off, and the precipitate washed with saturated zinc sulphate solution is then dissolved in the beaker in about 10 c.c. of concentrated sulphuric acid, and the nitrogen determined by Kjeldahl's method.

In most cases it will be sufficient to determine the total nitrogen and that precipitated by zinc sulphate only, the difference between the two being peptones and degradation products. If further differentiation is required, the filtrate from the zinc sulphate precipitate is heated with bromine as described above, and the nitrogen content of the precipitate found. The filtrate from this precipitate may be concentrated and Kjeldahled, or the lower nitrogenous bodies estimated by difference.

Chondrin.—There is still another constituent of glue generally present in small quantities, and sometimes sufficient to affect the quality of the glue and vitiate an analysis which neglects it. Though treatment of glue with zinc sulphate serves to differentiate true gelatin from allied bodies whose solutions have no consistency or adhesiveness, chondrin (a compound very closely akin to gelatin, but of only half its gelatinising power) cannot be thus separated. Chondrin, which is derived from cartilage, can be detected by adding alum or acetic acid to a solution of the glue, when the chondrin will coagulate, traces appearing as an opalescence. For estimation, the precipitate must be filtered off, washed with the precipitant, dried and Kjeldahled, the amount of nitrogen found multiplied by 6.89 giving the chondrin present. Instead of acetic acid potash alum may be used, when a little calcium chloride and sodium phosphate added to the solution will help the chondrin to coagulate and accelerate filtration. All the true gelatin should pass into the filtrate, but cannot be estimated there by the zinc sulphate method without considerable concentration; and this being likely to peptonise some of the gelatin, the latter should be determined together with the chondrin in a fresh portion of glue solution and the chondrin previously found deducted. The precipitated chondrin may, in some cases, contain mucin, which is derived from various animal secretions and causes the glue to froth badly. Mucin contains 13 per cent. of nitrogen. The mixed precipitate may be redissolved and treated with mercuric chloride or tannic acid, both of which precipitate chondrin but not mucin.

CHAPTER XX.

BENZINE.

THE solvents used in degreasing are generally derived from petroleum, but are met with under a variety of names, such as benzine, naphtha, etc. Gas-tar benzine is sometimes used, but is not much favoured on account of its smell and the somewhat bad colour of the residual grease. Carbon tetrachloride is also used as a solvent.

The requirements of different trades are slightly different, but it may be taken as a general rule that no benzine should be used which has large fractions distilling below 80° C. or above 110° C. The former fractions are difficult to completely condense, and, on account of their high vapour tension, a considerable volume is required to fill the apparatus with vapour. If present in any quantity, they further make it difficult to get the temperature of the extractor sufficiently high. The last runnings are very difficult to expel from the grease without overheating it, and so causing deterioration of colour together with increase of free acids and loss of glycerine; while, if they are left in, they increase the unsaponifiable matter and spoil the grease from a soap-maker's point of view. They are, moreover, apt to lag behind in the degreaser and do no work.

Experiments made by the author indicate that from every point of view the shorter the range of boiling points the better will the benzine behave, while, given a short range, it is better to have it fairly high. Thus a spirit, of which the bulk distils over between 90° and 110°, will be better than one between 80° and 100°. The power of dissolving grease increases with the mean molecular weight of the sample, although this must not be pushed too far, since any fractions above 120° require so much steam to expel that hydrolysis of the fat always occurs.

An ideal spirit for degreasing would be one with a constant boiling point of about 95° C., such as benzine C_6H_6 , which would, of course, be too dear. In the absence of such a liquid a benzine is judged by the portion distilling between a short range on either side of this point. The greater the percentage of a benzine that distils in the neighbourhood of 95° the better will be the sample, provided, of course, that the objectionable first and last runnings are absent or only present in insignificant quantities.

It is obvious that the testing of a benzine must be chiefly directed towards the above points—namely, the deterioration of the first and last runnings and the different fractions into which the remainder can be divided.

Other important tests are specific gravity, vapour tension, and, in the case of petroleum products, the presence or absence of benzol.

Specific Gravity.—This must always be determined in some form of stoppered bottle. The specific gravity of benzines ranges between 0.680 and 0.780. Although in a general way it gives some indication of the quality of the spirit, it does not necessarily follow that a spirit with a low gravity will contain a large proportion of low-boiling fractions.

Vapour Tension.—The determination of vapour tension is very useful (J. T. Wood, *J.S.C.I.*, 1904, p. 703), since the amount of incondensable vapour in a large plant depends directly upon this constant. The smaller the vapour tension the less spirit is lost in this way. The relative vapour tensions of different samples, which is in reality all that we require to know, may easily be determined by introducing some of each sample into a barometer tube filled with mercury under exactly the same condition and noting the depression of the mercury column.

Nitrication Test.—Petroleum products are sometimes partly or entirely replaced by benzols. Their presence may be detected by the production of nitrobenzine. Benzine, however, occurs sometimes naturally in small quantities in petroleum. If 5 c.c. of the spirit be added slowly to a mixture of nitric and sulphuric acids with constant shaking, and the mixture, after warming on the water-bath, be poured into water in the presence of benzine, drops of nitro-benzine will be observed and identified by their smell, or conversion into aniline by reduction with tin and hydrochloric acid.

The test may be made quantitative as follows (Allen, vol. ii., p. 162):—A flask is fitted with a cork, through which pass a stoppered tap funnel and a long tube to act as condenser. One hundred c.c. of the sample are placed in the flask, which has about 500 c.c. capacity. A mixture of 150 grms. of nitric acid (sp. gr. 1.4) and 180 to 200 grms. of sulphuric acid (sp. gr. 1.84) is prepared and cooled. This mixture is placed in the funnel and introduced into the flask in small quantities with continual shaking, the flask being at the same time kept cool, if necessary by immersion in water. When addition of acid produces no further rise of temperature the flask is connected to an inverted condenser and gently heated for an hour. After cooling, the mixture is poured into a separating funnel and the nitrobenzine separated. The acid layer is diluted with water, and any further nitrobenzine which separates added to the rest. The crude nitrobenzine is washed with dilute soda and water. The washed nitrobenzine is allowed to settle, carefully separated, and re-distilled in a fractionating flask until a temperature of 150° C. is reached. The distillate is again nitrated, using a large excess of the acid mixture. Any material remaining

undissolved is non-nitrifiable hydrocarbon. 157.6 parts of nitrobenzine correspond to 100 parts of benzine.

Distillation Test.—Although this test is of supreme importance, there is at present no standard method of carrying it out which is generally accepted by both buyers and sellers. In view of the great effect of varying conditions on a fractional distillation, this is particularly unfortunate.

It has already been mentioned that for degreasing plants, benzines should contain but a small fraction boiling below 80° C. or above 110° C. while of the other fractions the largest should boil between 90° C. and 100° C. A distillation test should, therefore, be specially directed to those two points. The test, as ordinarily carried out by the trade, may be regarded as absolutely useless for the purpose of detecting the lower fractions. It is merely a distillation without any real attempt at fractionation. The apparatus generally used consists of a distilling flask of about 2 $\frac{3}{4}$ in. in diameter with a neck of $\frac{3}{4}$ in., the distance from the shoulder or top of the globular portion to the lateral exit tube for vapour being 2 $\frac{1}{2}$ in. A thermometer with a cylindrical bulb is inserted through the cork and the lateral tube is connected with a Liebig condenser 24 in. long.

One hundred c.c. of the benzine is measured into the flask and the thermometer so adjusted that the bulb is half immersed in the liquid. The flask is then connected to the condenser and an Argand burner placed underneath. The distillate is collected in a graduated 100 c.c. cylinder.

A small flame is placed under the flask and the temperature at which active ebullition occurs is noted. The flame is then extinguished and the thermometer bulb raised to a position 1 in. below the exit tube. The gas is relighted and thermometer readings taken as each 10 c.c. of distillate is collected in the measure glass. The final temperature is that when 95 per cent. of the liquid has been collected. The rate of distillation is regulated so that the distillate drops from the condenser in drops as fast as possible without forming a stream. The whole experiment should occupy about 30 minutes. If these conditions be carefully observed consistent results will be obtained, but results which, for degreasing purposes, are of very little value, as the test is obviously crude and unscientific. The only point in its favour is its simplicity.

By substituting some form of dephlegmator useful results are obtained, and it is remarkable that an admittedly antiquated method has so long been recognised. Of course, initial difficulties may arise in the selection of a method, since, as is well known, many conditions affect the results of practical distillation; but the method described above is open to all these objections to quite as great an extent. The retention of such a test is an illustration of the misapplication of standardisation or of standardisation which is not subject to constant criticism and revision.

Garry and Watson (*J.S.C.I.*, 1904, 701) have called attention to the unsatisfactory condition of benzine testing and given many results of different tests, all of which prove that some form of standard apparatus and condition of working must be adopted between buyer and seller.

A very simple and efficient method, which is used by the author, is the following (*J.S.C.I.*, 1906, 1202):—

A round flask of 150 c.c. capacity and having a neck about 3 in. in

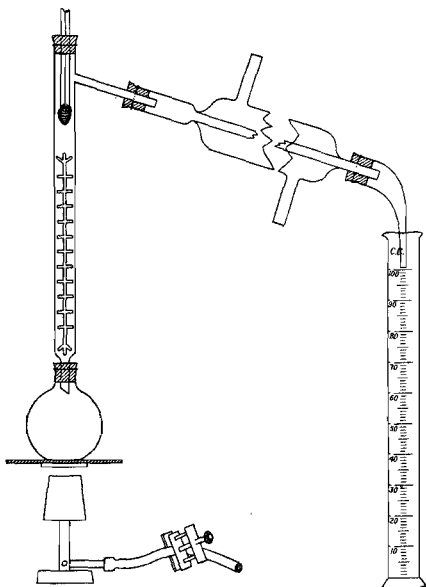


FIG. 47.

length is fitted to a Young's rod and disc fractionating column, containing sixteen chambers, the distance from the neck of the flask to the lateral exit being 13 in. (fig. 47). The thermometer bulb is placed about 1 in. below the lateral tube, which is connected to a Liebig condenser, with an adapter leading into a graduated 100 c.c. cylinder. One hundred cubic centimetres of the benzine are placed in the flask, which is then connected up and

placed on a piece of asbestos with an annular hole about 1 in. in diameter. The liquid is heated with a small bunsen burner protected by a shade, the height of the flame being regulated by means of a screw clamp. The distillation is conducted at the rate of about 2 drops a second and the readings taken at intervals of 10° C. The distillation is started with a flame sufficiently large to give the required rate of distillation, and is only altered when either this or the temperature shows any signs of falling. The distillate is collected in a graduated glass cylinder, which should be stood in cold water of the same temperature as the benzine when measure^d into the flask. The volume of the distillate is read at each ten degrees, including in the reading all that will come over at that particular temperature. It is convenient to commence reading at 70° C., and to continue at intervals of 10° up to 110° or 120°. In each case the reading is taken the moment the mercury thread appears above the mark. Having obtained these volumes it is easy to obtain the fractions distilling between each successive 10°. Thus:—

Volume at 80° C.	20
Volume at 90° C.	55

∴ fraction distilling between 80° and 90° C. = 35.

The method is capable of giving perfectly consistent results. This may be seen from the following table, which gives the figures obtained independently by three different persons from the same benzine, and in column 4 are the results of the trade test upon the same sample.

TABLE LX.

	1	2	3	4
Fraction up to 70°	2·5	2·5	2·5	0·0
„ between 70°-80°	21·5	20·5	22·0	5·0
„ „ 80°-90°	31·0	32·0	31·5	45·0
„ „ 90°-100°	24·0	23·5	22·0	35·0
„ „ 100°-110°	13·0	13·0	13·5	11·0
„ above 110°	8·0	8·5	8·5	4·0

An inspection of these figures will at once show the extreme difference between the two methods. If the sample be judged upon the trade test it is an uncommonly good one, while, in reality, it should be condemned. The above method was adopted as one simple to work, not requiring very delicate apparatus, and giving results comparable with practical experience. It is, of course, necessary that both buyer and seller should use the same test and that the conditions of experiment should be carefully defined. It should not be difficult to do this, if the question were treated in the same progressive manner as the analysis of tanning materials by the I.A.L.T.C. The persistent retention of a method which is admittedly

unscientific and has been proved to be inaccurate cannot be too strongly condemned. The following examples of good and bad benzines may be given :—

TABLE LXI.

		Good.	Bad.	
Fractions distilling up to	80°	3·0	25·0	6·0
" "	between 80°-90°	12·0	33·0	14·0
" "	" 90°-100°	82·0	16·0	33·0
" "	" 100°-110°	3·0	14·0	26·5
" "	above 110°	0·0	12·0	20·5

CHAPTER XXI.

DYESTUFFS.

Determination of the Nature of a Dyestuff.—To determine whether the dye is homogeneous, a pinch of it, dry and powdered, may be blown from a distance on to a piece of filter paper moistened with water or alcohol. The scattered particles falling on the wet surface will, if soluble, dissolve and, if of different dyes, stain the paper with spots of their respective colours. To distinguish dyes which, though chemically different, give the same shade of colour in solution, some of the sample must be blown on to a white porcelain surface moistened with strong sulphuric acid, alcohol, etc., and any difference of effect observed. In the case of very intimate mixtures, such as result from the evaporation of a mixed solution, particles of the component dyes cannot be mechanically separated. Such mixtures require another method. A solution of the dyestuff is made, and pieces of fibre are dyed in it successively until it is exhausted. If the dyestuff is not homogeneous the fibres will exhibit different colours, since scarcely any fibre has the same affinity for different dyes.

From a mixture containing both a basic and an acid dyestuff the free base of the first can be extracted from an alkaline solution of the mixture with ether or wool. The acid dyestuff remains in the aqueous solution, and, after acidifying with a stronger acid, the colour acid can then be extracted in the same way.

Classification of Dyestuffs.—Dyestuffs have been divided into several large classes, according to their behaviour with some of the most general reagents. Green has grouped the dyestuffs most likely to be used for leather into those which are soluble and those which are insoluble in water, dividing the soluble dyestuffs again into basic colours which are precipitated, and acid colours which are not precipitated by tannin solutions; with further sub-division of each, according as the dyestuffs (after reduction with zinc and hydrochloric acid) regain their colour quickly, slowly, or not at all. In another, Rota's scheme of analysis, the first classification is into dyestuffs reducible and dyestuffs non-reducible with stannous chloride and hydrochloric acid. One part of the dyestuff is dissolved in 1000 parts of water or alcohol, or, if insoluble, suspended in

the liquid. Five c.c. are mixed with 4 or 5 drops of hydrochloric acid, and the same quantity of 10 per cent. stannous chloride solution shaken and, if necessary, boiled. If decoloration is imperfect, more stannous chloride is added. If reducible, the decolorised solution is neutralised with KOH or sodium acetate and treated with ferric chloride solution or air.

Class 1. The solution remains colourless, showing that the dyestuff is not re-oxidised after reduction. Of this class are the nitro-, nitroso-, and azo-dyestuffs, such as Picric Acid, Fast Green O, and Chrysoidine.

Class 2. The solution becomes coloured again, showing that the dyestuff is re-oxidised after reduction. Such are Meldola's Blue, Methylene Blue, and quinone-imido derivatives.

If the dyestuff is unchanged by the reducing mixture, treat a portion of the original solution with a 20 per cent. solution of potash, and warm.

Class 3. The solution is decolorised or a precipitate forms. Of this class are the imidocarboquinone dyestuffs, including Auramine, Magenta, Quinoline Yellow.

Class 4. The solution becomes intensely coloured and no precipitate is formed. Oxycarboquinone dyestuffs—Aurine, Eosine, Alizarin.

Further division into single families is based on the different nature of the salt-yielding groups in the dyestuffs. The presence of amido or imido-groups, carboxyl or sulphonic groups, if proved, will further limit the field of inquiry. The class to which a dyestuff belongs having been determined, some of the special tests which serve to distinguish typical dyes should be applied, when, possibly, its relationship to a well-known type may be established.¹ Some of these typical dyes and their reactions are given later, but for a complete list, *Synthetic Dyestuffs*, by Cain and Thorpe, should be consulted.

Halogens and sulphur should be tested for, as their presence in dyes of certain classes simplifies further examination.

To detect halogens the dye may be treated in the usual way of testing for the elements in organic substances, heating with lime or sodium. Or, instead, the solution of the dyestuff can be boiled with zinc dust and potash, the solution filtered, acidified with acetic acid, and tested with chlorine water and starch solution. Sulphur is detected by fusing the dyestuff with potassium nitrate and testing the filtered solution of the melt for sulphuric acid.

In those dyestuffs which are reduced by stannous chloride an examination of the products of decomposition will help identification. Compounds which contain the azo-groupings, often give, on reduction, two primary bases or their derivatives. If the excess of tin be precipitated with sulphuretted hydrogen and the filtrate made alkaline with potash a mixture of the free bases will be obtained, from which the base that is not sulphonated may be extracted with ether. A sulphonated base remains in the aqueous liquor, and can often be recognised by the characteristic dyestuff it gives with certain diazo-salts.

The Analysis of Dyestuffs.—Dyestuffs being of a complex nature,

¹ *J.S.C.I.*, 1898, 798.

and often mixtures, are very difficult to analyse readily, the analysis being often complicated by the presence of such substances as glucose, sodium sulphate, etc. Perhaps the best test by which they can be compared is a trial dye experiment. In many cases a test of a tincture or solution of the dye by means of the tintometer will be sufficient for comparative purposes. In either case, however, one can only effect a comparison between two or more samples of one and the same dye or two or more similar dyes. Minute differences in the intensity of two dyeings can only be determined in light shades. In examining yellows it is advisable to combine the dye with another, such as a blue.

The following method of colorimetric estimation may be employed:—The instrument used is due to C. H. Wolff, and “depends on the fact that light rays suffer a diminution in brightness in passing through a stratum

of coloured liquid, the decrease being in proportion to the degree of concentration of the liquid, *i.e.* the greater the quantity of dye in the liquid the more will the light be dimmed in passing through.”

The following description of the instrument is taken from Georgievics' *Chemical Technology of Textile Fabrics*, p. 226:—

B and C (fig. 48) are tubed cylinders into which the dye solutions are poured; A is a reflector; D a pair of prisms, which so unite the two bundles of light rays in the field of vision of the lens E that the one half of the circular field of vision corresponds to the light transmitted through the one prism, and the other half to the rays traversing the other prism.

The two solutions for comparison, which must be very dilute, are placed in the respective cylinders and examined, the darker one being reduced in volume by drawing it off through the lateral tap until both sides of the field of vision appear of equal intensity of colour.

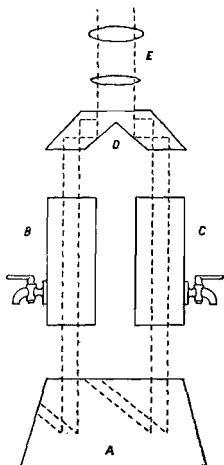


FIG. 48.

Now the capacity of absorption for light is inversely proportional to the thickness of the absorbent layer traversed by the rays. Thus, for example, if to produce equal intensity in the two halves of the field it is necessary to reduce the one liquid to half the volume of the other liquid, then the absorptive capacity of the former will be double that of the latter. As, now, the absorptive capacity of a liquid for light depends directly on the degree of concentration, then, by assuming the height

of the two columns of liquid in the test cylinders as being represented by $H H'$, whilst the concentration of the liquids is expressed by $C C'$, we obtain the following simple relation :—

$$C : C' :: H' : H.$$

The relative colour strength of the solutions under examination can be easily calculated by the aid of the proportion.

In making a determination it is not advisable to confine the examination to a single test, but to make at least two, and to repeat these after reversing the two cylinders, the arithmetical mean of the four tests being taken to express the result.

Sample Dyeings are carried out by taking 1 grm. of the dyes and dissolving it in a litre of water. These solutions are then employed to dye equal weights of suitable material under exactly similar conditions. After dyeing, the fabrics are washed and dried, and the resulting difference determined with reference to the amount of dye consumed. If the baths have been imperfectly exhausted, another dyeing should be made, as it is essential that at the end of the experiment the concentrations of the two baths should be the same. If, during the process of dyeing, a considerable difference exists between the samples, the weaker bath should be strengthened with more of the dye solution. If the dyes be mixtures, it will become apparent during the experiment, owing to the selective absorption of the material for the constituents of the mixture. The dye-pots may be easily kept at a constant temperature by immersing them in a bath of glycerine or brine.

The following points in connection with the dye are then investigated :—

(1) *Solubility in Water*.—This may be determined by making a saturated solution, evaporating a portion to dryness, and weighing the residue. Since many dyes are precipitated by lime, it is advisable to make a second experiment with the water that will be used, and, if necessary, correct for this by the addition of sufficient acid or alkali to prevent this precipitation.

(2) *Equalising Power*.—This depends upon the affinity of the fibre for the dyestuffs, some being more rapidly absorbed than others. The too rapid absorption of a dye may be prevented by the addition of sodium sulphate to the bath. Georgievics¹ determines the equalising power of a dyestuff as follows :—A sample of the material is taken and a portion of it bound so that it does not come in contact with the dye solution; the sample is then dried till equilibrium is established. The bound portion is then untied and the material again immersed in the bath. It now absorbs dye until equilibrium is set up, in accordance with the law of distribution. The bath is at the same time weakened, and the equilibrium between it and the rest of the stuff is disturbed, the result being that a portion of the dye is removed from the portions previously dyed. If the dye has good equalising powers, the new portion will

¹ *Chemical Technology of Textile Fibres.*

quickly assume the same colour as the unbound portion. If, however, the equalising power is low, it will assume a lighter shade.

Fastness.—In the case of leather, fastness to light is very important. It may easily be tested by placing a piece of the leather in a photographic printing frame and covering half of it, the frame then being exposed to sunlight. The colours of the two halves are compared frequently and any change noted. Very fast dyes will stand exposure for a month in summer without appreciable change. It is, of course, important that, during exposure to light, no acid or alkali should be present. The action of acids and other reagents, into contact with which leather is likely to come, can readily be tested in a similar manner. In testing fastness to perspiration dilute acetic acid may be used.

The impurities present in dyestuffs may be tested by the ordinary methods. A determination of moisture and ash should be included, and sodium chloride and sulphate, magnesium sulphate, alkaline carbonates, and zinc looked for. An aqueous solution should be tested for dextrin, sugar, etc.

In the case of basic dyestuffs an aqueous solution is precipitated with ammonia, the precipitate filtered off and the acid tested for in the filtrate. *The acid dyestuffs*, on the other hand, may be treated with hydrochloric acid and filtered, the base being tested for in the filtrate.

The Recognition of Dyestuffs.—From an investigation of the different schemes constructed for the identification and classification of organic dyestuffs, Galinow (*J.S.C.I.*, 1906, p. 1007) concludes that the most satisfactory method of analysis is that based on the reduction of the dyestuff with either zinc dust in acid or alkaline solution or stannous chloride and hydrochloric acid. The behaviour with other reducing agents has also been studied by the same author, the results being given in the following tables. Thus zinc dust in neutral solution and hydrosulphite NF have been employed in determining to what chemical group a dyestuff belongs, whilst to ascertain the chemical properties the ether reaction was found to furnish useful information. In carrying out the scheme the unknown dyestuff is in the first place examined for the presence of a sulphur group. Some sulphur dyestuffs may be recognised by their physical properties, such as imperfect solubility and evolution of hydrogen sulphide, while others are completely soluble in water, fail to liberate sulphuretted hydrogen, or exhibit an alkaline reaction and give a precipitate with tannin. As dyestuffs in the form of bisulphite compounds react with lead paper, a test for the presence of sulphurous anhydride should always be made. If the dyestuff does not belong to the sulphur or oxyketone groups, it is further investigated for solubility and the solution reduced with zinc dust and hydrochloric acid. If a precipitate is produced the reduction is carried out in alkaline solution. The reduced solution is filtered and oxidised with persulphate to ascertain whether the dyestuff can be regenerated.

As a general rule the recognition of a dye will have to be made with a dyed fibre or skin. The dye may be extracted with alcohol or a suitable solvent, and tested, but it is better to treat small portions of the material in a porcelain dish with certain reagents and note the reaction, comparing it with the tables.

The following tables (LXII., pp. 262-278) are taken from Cain and Thorpe's *Synthetic Dyestuffs and Intermediate Products*, which should be consulted for further information. When possible it is always better to strip the dye from a leather and to re-deposit it on a little pure wool.

The following are the reagents used :—

- (1) Concentrated sulphuric acid.
- (2) Ten per cent. sulphuric acid.
- (3) Concentrated hydrochloric acid.
- (4) Ten per cent. hydrochloric acid.
- (5) Nitric acid of specific gravity 1.40.
- (6) Ammonia of sp. gr. 0.91.
- (7) Ten per cent. sodium hydrate.
- (8) Stannous chloride and hydrochloric acid solution, containing—

100 grms.	SnCl ₂ .
100 „	HCl.
50 „	water.

A. G. Green (*J.S.C.I.*, 1905, 1034) uses the following method for recognising dyes on animal fibres,¹ depending on the behaviour of different reduction products on oxidation.

He uses the following reagents :—

- (1) Dilute ammonia (1 in 100).
- (2) Aqueous alcoholic ammonia, containing 1 c.c. of ammonia, 50 c.c. of alcohol, and 50 c.c. of water.
- (3) Five per cent. acetic acid.
- (4) Fifty per cent. alcohol.
- (5) Dilute hydrochloric acid (1 in 10).
- (6) Ten per cent. caustic soda.
- (7) Hydrosulphite A (10 per cent. solution) or formaldehyde sodium hydrosulphite.
- (8) Hydrosulphite B (200 c.c. of hydrosulphite A and 1 c.c. of glacial acetic acid).
- (9) Cold saturated potassium persulphate.
- (10) Five per cent. solution of crystallised sodium acetate.

The tests are carried out as follows :—

“The reactions are performed in test-tubes with pieces of the material about $\frac{1}{2}$ in. to 1 in. square, which are covered with about 1 in. to $1\frac{1}{2}$ in. of the reagent. In making ‘stripping tests’ the degree of stripping is judged by comparing the depth of shade remaining with that of the

¹ The tests given are for wool.

CAIN AND THORPE'S TABLES.
TABLE LXII.—BLACK, VIOLET, AND BLUE DYE-STUFFS.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2$ + HCl.
Indigo (vat blue) (wool),	F, olive green; after addition of water, light blue. S, first yellow, then olive and green, lastly deep blue.	Unchanged.	Unchanged.	—	Yellow with green rim.	Unchanged.	Unchanged.	On heating, F, lighter; S, greenish-yellow.
Alizarin blue (chromium mordant) (wool),	F, little changed. S, dirty grey.	—	F, little changed, S, dirty red.	—	Olive-brown.	F, green-blue; S, —	F, dark green-blue; S, —	Dirty olive-yellow.
Diamond black with chrome mordant (wool),	F, greener. S, blue-green; on dilution, violet.	—	F, dark blue-green. S, colourless.	—	Dark red.	F, — S, blue-grey.	F, darker. S, blue-grey.	Decolorised.
Gallæine (chromium mordant) (wool),	F, dark brown. S, brownish.	Red violet.	F, dark red. S, amber-yellow.	—	Yellow.	F, no change. S, —	F, bluer. S, —	Brown-red.
Gallocyanine (chromium mordant) (wool),	F, bluer. S, deep blue; on dilution, red.	F, little changed. S, weak violet.	F, violet. S, violet.	—	Red-brown.	F, — S, —	F, dirty purple. S, —	—
Alizarin blue S (chromium mordant) (wool),	F, greener. S, deep green-blue.	No change.	F, redder. S, light red.	—	Yellow with violet rim.	F, little change. S, —	F, blue-green. S, colourless.	Dark violet.
Brilliant blue G (chromium mordant) (wool),	F, greenish-yellow; on dilution, violet to blue. S, green.	—	F, bright green; on dilution, violet. S, —	—	Yellow.	F, greenish-blue. S, —	F, green-blue. S, colourless.	Decolorised.

Alizarin indigo blue (chromium mordant) (wool),	F, darker. S, dark reddish-blue.	—	F, slightly darker. S, rose-coloured.	—	Dirty yellow with violet edge.	F, greener. S, —	F, greener. S, colourless.	—
Chrome violet (By) (chromium mordant) (wool),	F, orange-yellow. S, yellow.	—	F, bright carmine. S, rose-coloured.	—	Yellow with red edge.	F, lighter. S, —	F, on standing, lighter. S, —	—
* Patent blue (silk),	Green, then yellow.	Green.	Yellow.	Green, then light yellow.	Yellow.	Slightly weakened.	Slightly weakened.	Blue-green.
* Patent blue A (silk),	Green, then yellow.	Little change.	Green, then yellow.	Grass green.	Green, immediately yellow.	Darker.	Darker.	Green, changing to yellow.
* Patent blue V (silk),	Green, then brown-yellow.	Green.	Green, then yellow.	Green, then yellow.	Green, immediately yellow.	Slowly decolorised.	Slowly decolorised.	Bluish-green.
Naphthol black B (wool),	F, dark blue-green. S, green-blue.	Little change.	Little changed.	—	Red.	F, blue-violet. S, violet.	F, little changed. S, —	Carmine.
Red violet 4RS and 6RS (wool),	F, yellow. S, yellow.	Brighter.	F, nearly decolorised. S, —	—	Bright yellow.	F, decolorised. S, —	F, decolorised. S, —	Little changed.
Acid violet 2B (wool),	F, yellow. S, yellow.	Greenish-yellow.	F, greenish-yellow. S, —	—	Yellow with green-blue edge.	F, decolorised. S, —	F, nearly decolorised. S, —	Blur.
Acid violet 4BN (wool),	F, red-yellow. S, yellow.	Brighter.	F, bright yellow. S, yellow.	—	Yellow with greenish edge.	F, decolorised; colour returns in the air. S, —	F, decolorised. S, —	Blue-green.
Formyl violet S 4B (wool),	F, red-yellow. S, yellow.	No change.	F, yellowish-green. S, yellowish-green.	Green.	Green.	Blue.	Light grey.	Red-brown.

* F = fibre.
 ** Indicates colours investigated by Guehm and Surbech.
 † S = solution.
 ‡ Indicates colours investigated by Lange and Guehm.
 *** Indicates colours investigated by Heermann.

TABLE LXIII.—BLACK, VIOLET, AND BLUE DYE-STUFFS—continued.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2$ + HCl.
Fast acid violet 10B (wool).	F, green, then yellowish-green. S, yellowish.	Bright blue-green.	F, bright green, then amber-yellow. S, yellowish.	—	Green, with greenish-yellow edge.	F, light blue. S, —	—	—
Alkali violet (wool).	F, bright orange. S, yellow.	Blue-green.	F, bright orange. S, yellow.	—	Yellow.	F, colourless. S, —	F, colourless. S, —	Blue-green.
Violamine R (wool).	F, red. S, dirty red.	—	F, bluer. S, rose.	—	Scarlet.	F, rose. S, —	F, cherry-red. S, —	Bluer.
Violamine B (wool).	F, bright scarlet. S, red.	—	F, blue violet. S, —	—	Bright scarlet.	F, redder. S, rose.	F, red-violet. S, —	—
Water blue (wool).	F, red. S, red.	No change.	F, brighter. S, light blue.	—	Green.	F, decolorised. S, —	F, light brown-red. S, —	Little changed.
Cyanine B (wool).	F, green, then dirty yellow. S, —	Bright green-blue.	F, bright green-blue. S, —	—	Yellow with green rim.	F, brighter. S, weak blue.	F, olive-green. S, —	—
Fast acid blue B (wool).	F, light brown; on dilution, blue. S, light brown; on dilution, light blue.	Little change.	F, yellow; on dilution, blue. S, —	—	Yellow-green.	F, little changed. S, —	F, light blue-green. S, colourless.	Green.

Induline NN (soluble) (wool),	F, brighter and redder. S, blue; on dilution, violet.	Little change.	F, brighter. S, light blue.	—	Dark violet	F, little change. S, colourless.	F, red-violet. S, colourless.	Little change.
Nigrosine (soluble) (wool),	F, dark violet. S, blue.	—	F, darker. S, reddish-blue.	—	—	F, maroon. S, —	F, dirty maroon. S, —	—
Methyl violet B (wool),	F, orange; colour returns on dilution. S, yellow.	F, blue-green. S, green-blue.	F, orange; colour returns on dilution. S, yellow.	—	Yellow with green edge.	F, nearly decolorised. S, —	F, decolorised slowly. S, —	Blue-green.
Toluidine blue (wool),	F, dark olive-green. S, greenish.	F, no change. S, light blue.	F, slight change. S, blue.	—	Olive-green.	—	F, carmine. S, —	Decolorised.
Nile blue (wool),	F, red. S, brown.	F, greener. S, light yellow.	F, green-yellow. S, green-yellow.	—	Brown-yellow with green edge.	F, dark violet. S, —	F, deep carmine. S, —	—
Paraphenylene blue (wool),	F, darker. S, blue.	—	F, darker. S, blue.	—	Green-yellow.	F, violet. S, —	F, purple. S, —	Lighter.
Indamine blue B (wool),	F, much darker. S, bright blue.	Darker.	F, darker. S, bright blue.	—	Green.	—	F, purple. S, —	—
Indoine blue (wool),	F, dark olive-green; on dilution, blue-violet. S, olive-green.	—	F, blue-green. S, —	—	Bright yellow-green.	—	F, on standing, violet. S, rose.	Greener.
** Indoine blue 2B (taunised cotton),	Greenish-yellow.	—	—	Green.	Dark green.	—	S, light yellow.	Unchanged.

TABLE LXII.—BLACK, VIOLET, AND BLUE DYESTUFFS—continued.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2 + HCl$.
Maddala's blue (cotton).	F, black ; colour returns on re-tinture on dilution.	—	F, violet-grey ; S, reddish.	—	F, violet. S, violet.	F, dark red-brown. S, weak brownish.	F, dark red-brown. S, light brownish.	First green, then slowly decolorised.
Violet black (cotton).	F, deep blue. S, blue.	Little changed.	F, blue. S, colourless.	—	Red-orange.	F, little changed. S, violet.	F, little changed. S, rose.	Decolorised.
Benzo black S extra (cotton).	F, dark violet. S, violet.	Green.	F, dark violet. S, colourless.	—	Yellow-red.	F, red-violet. S, rose.	F, red-violet. S, weak red.	Decolorised.
Benzo grey S extra (cotton).	F, dark violet. S, green-blue.	Green.	F, blue. S, colourless.	—	Yellow-red.	F, redder. S, —	F, red-violet. S, colourless.	Decolorised.
* Vidal black (cotton).	Green-black.	No change.	Little change.	No change.	Becomes grey.	No change.	Becomes blue-green.	Dirty yellow-brown.
* Immedial black V extra (cotton).	Blue-grey.	No change.	Little change.	No change.	F, brownish. S, claret-red.	No change.	No change.	Decolorised.
* Immedial blue C (cotton).	Unchanged.	—	—	Unchanged.	Green.	—	Unchanged.	Unchanged ; on boiling, blue.
Congo Corinth G (cotton).	F, deep blue. S, blue.	Blue.	F, blue. S, colourless.	—	Brown.	F, brighter. S, rose.	F, redder. S, colourless.	Decolorised.
Azo-blue (cotton).	F, green-blue. S, blue.	Little changed.	F, little changed. S, —	—	Orange.	F, red-violet. S, rose.	F, magenta-red. S, rose.	Decolorised.

DYESTUFFS.

Benzoearnine G (cotton),	F, green-blue, S, blue.	Redder.	F, little changed. S, —	—	Light brown.	F, red-violet, S, rose.	F, carmine, S, pale rose.	Decolorised.
Diamine blue 3R (cotton),	F, green-blue, S, blue.	Little changed.	F, darker. S, colourless.	—	Orange-yellow.	F, red-violet, S, rose.	F, Magenta-red, rose.	Decolorised.
*** Chromotrope FB, after-chromed (wool),	L, bluish; on dilution, red-violet.	Unchanged.	Almost un-changed.	Unchanged.	F, slightly browner.	Unchanged.	F, redder. S, reddish.	Almost un-changed.
*** Acid alizarin blue BB (wool) after treated with chromium fluoride,	S, dirty blue; on dilution, red-violet.	Unchanged.	Almost un-changed.	Unchanged.	Almost un-changed.	Unchanged.	Unchanged.	Unchanged.
*** Fast blue 2B (wool),	F, almost black. S, violet-black. On dilution, S, intense blue; F, almost colourless.	Almost un-changed.	S, blue.	Almost un-changed.	S, dirty blue.	F, blue-violet.	F, violet.	F, dark blue-green; on dilution, blue.
*** Sulphur blue L extra, after-chromed (wool),	L, violet-black; on dilution, dirty violet.	F, slightly browner.	F, dark brown. S, light yellow.	F, brown.	F, brown-red. S, violet.	F, darker.	F, darker.	F, quickly dirty brownish-yellow.

Note.—Heermann, who has investigated the dyestuffs marked (***) recommends the use of nitric acid, sp. gr. 1.3, and ammoniac, sp. gr. 0.925 (20 per cent. solution), instead of the strengths given above.

TABLE LXII.—YELLOW AND ORANGE DYE STUFFS.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2 + HCl$.
Gallophane (chrome-mordanted wool).	Indefinite.	Little change.	F, greener. S, light yellow	—	Yellow.	F, little changed. S, colourless.	F, slightly darker. S, light yellow.	Lighter.
Alizarin A (chrome-mordanted wool).	F, dark yellow. S, pale yellow.	—	F, little changed. S, —	—	Green-yellow.	F, darker. S, —	F, darker. S, —	—
Milling yellow (chrome-mordanted wool).	F, brilliant, red-orange; S, red-orange; on dilution, light yellow.	No change.	F, carmine. S, red-orange.	—	Orange.	F, redder. S, —	F, browner. S, bright yellow.	Decolorised.
Diamond yellow G (chrome-mordanted wool).	F, dark orange-red. S, —	Light red-brown.	F, dark orange-red. S, light yellow	—	Brilliant orange-red.	F, slightly darker. S, —	F, slightly darker. S, —	Light red-brown.
Alizarin orange (chrome-mordanted wool).	F, darker. S, light brown.	F, little changed. S, slightly darker.	F, lighter. S, yellow.	—	Dirty yellow.	F, redder. S, —	F, redder. S, —	Little action.
*Moriant yellow (wool).	Red.	No change.	Red-brown.	Redder.	Brown-red.	Little change.	Orange.	Redder.
Pteric acid (wool).	F, indefinite; colour returns on dilution. S, on dilution, yellow.	F, little changed. S, light yellow.	F, decolorised. S, —	—	Straw yellow.	F, orange. S, yellow.	F, orange. S, yellow.	Lighter.
Xanthol yellow (Marras yellow wool).	F, decolorised. S, —	Lighter.	F, decolorised. S, —	—	—	F, lighter. S, yellow.	F, little changed. S, yellow.	Decolorised.

Naphthol yellow S (wool).	F, browner. S, colourless.	Lighter.	F, decolorised. S, —	—	Browner.	F, bright. S, yellow.	F, little changed. S, yellow.	Decolorised.
Fast yellow G (wool).	F, bright terra-cotta. S, yellow.	F, orange; on standing, bright scarlet. S, rose.	F, scarlet. S, red.	—	Yellow with bright red edge.	F, little action. S, yellow.	F, darker. S, yellow.	Decolorised.
Azoflavine (wool).	F, red-violet. S, —	Darker.	F, red violet. S, carmine.	—	Red with purple edge.	F, little action. S, —	F, greener and darker. S, —	Lighter.
Metanil yellow (wool).	F, dark purple. S, —	Brown-red, becoming purple.	F, bright purple. S, reddish-purple.	—	Red with purple edge.	F, little action. S, —	F, brighter. S, —	Brown, becoming purple.
Methyl orange (wool).	F, carmine. S, —	Carmine.	F, carmine. S, rose.	—	Yellow with carmine edge.	F, little action. S, —	F, little action. S, —	—
Orange II. (wool).	F, bright scarlet, becoming carmine. S, scarlet.	—	F, scarlet to carmine. S, rose.	—	Yellow with scarlet edge.	F, darker. S, light orange.	F, scarlet. S, —	—
Orange G (wool).	F, carmine. S, red.	Little action.	F, scarlet. S, rose.	—	Yellow with red edge.	F, no action. S, —	F, terra-cotta. S, —	Decolorised.
Orange R (wool).	F, carmine. S, red.	—	F, scarlet. S, rose.	—	Yellow with red edge.	—	F, terra-cotta. S, —	—
Tantrazine (wool).	F, darker. S, bright yellow. low.	No change.	F, slightly darker. S, yellow.	—	Orange.	F, brighter. S, light yellow.	F, redder. S, bright yellow. low.	Lighter, slowly decolorised.
Quinoline yellow (wool).	F, reddish-yellow. S, pale yellow.	—	F, amber-yellow. S, pale yellow.	—	—	F, no change. S, —	F, weaker. S, —	Slightly brighter.

TABLE LXII.—YELLOW AND ORANGE DYE-STUFFS—continued.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl .	10 per cent. HCl .	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. $NaOH$.	$SnCl_2$ + HCl .
Uranine (Fluorescine) (wool).	F, green-yellow. S, green-yellow.	F, lighter. S, yellow.	F, brighter. S, yellow.	—	No change.	F, redder. S, deep yellow with strong green fluorescence.	F, orange-yellow. S, yellow with strong fluorescence.	Little change.
Phosphine (wool).	F, dirty green-yellow. S, light yellow.	Orange.	F, brighter and lighter. S, yellow.	—	Little changed.	F, little changed. S, _____	F, yellow. S, _____	Nearly decolorised.
Chrysoidine R (wool).	F, yellow-brown. S, yellow.	Orange.	F, scarlet. S, rose.	—	Orange-red.	F, yellow. S, _____	F, deeper. S, _____	Orange.
Thioflavine S (wool).	F, brown; on standing, colourless. S, _____	Lighter.	F, decolorised. S, _____	—	—	F, lighter. S, _____	F, much lighter; on standing, colourless.	Brighter.
*Acridine yellow (wool).	Green-yellow.	Little change.	Red.	Little change.	Brown.	Little change.	Pale yellow.	Redder.
*Acridine orange (wool).	Green-yellow.	Redder.	Green-yellow.	Red.	Yellow.	Greenish-yellow.	Greenish-yellow.	Yellowish.
Benzoflavine (cotton).	F, much lighter. S, _____	No action.	F, orange. S, _____	—	—	F, lighter. S, _____	F, lighter. S, _____	Decolorised.
Auramine O (cotton).	F, olive-yellow. S, on dilution, yellow.	Lighter.	F, lighter. S, _____	—	Brownish.	F, lighter. S, _____	F, lighter. S, _____	Decolorised.
*Thioflavine T (cotton).	F, light red. S, colourless.	Orange.	F, brighter. S, yellow.	—	Brown.	F, no action. S, _____	F, no action. S, _____	Brown.
Chrysamine G (cotton).	F, carmine. S, red-violet.	Lighter.	F, carmine. S, colourless.	—	Violet-brown.	F, orange. S, _____	F, orange. S, _____	Decolorised.

Carbazol yellow (oot-ton),	F, dark green-blue. S, blue.	Olive-green.	F, violet. S, colourless.	—	Carmine.	F, slightly redder. S, colourless.	F, red-orange. S, rose.	Decolorised.
Brilliant yellow (oot-ton),	F, red-violet. S, red.	Browner.	F, red-violet. S, —	—	Dark purple.	F, scarlet. S, rose.	F, scarlet. S, rose.	Decolorised.
Chrysohemine (oot-ton),	F, red-violet. S, violet.	Little change.	F, violet. S, colourless.	—	Violet.	F, no change. S, —	F, no change. S, —	Decolorised.
Primaline (cotton),	F, weaker. S, pale yellow.	Orange.	F, orange. S, yellow.	—	Yellow.	F, no action. S, —	F, orange. S, —	Yellow.
Primaline with resorcinol (cotton),	F, carmine. S, red.	Redder.	F, dark red. S, red.	—	Dark red.	F, darker. S, —	F, dark red. S, —	Dark red.
*Alizarin yellow A (cotton),	Dirty yellow-green.	No change.	Paler.	No change.	Yellowish.	Browner.	Browner.	Colourless.
Congo orange B (oot-ton),	F, deep blue. S, blue.	Brown.	F, violet. S, —	—	Carmine.	F, no action. S, —	F, no action. S, —	Carmine.
Benzo orange B (oot-ton),	F, blue. S, blue.	Green-blue.	F, blue. S, colourless.	—	Brown.	F, scarlet. S, colourless.	F, carmine. S, colourless.	Brown.
***Immedial yellow D (cotton),	S, yellow-grey; on dilution, yellow.	F, slightly redder.	F, slighter darker red.	F, slightly darker.	F, darker brown.	Unchanged.	Unchanged.	F, browner.
***Immedial orange C (cotton),	S, brown; on dilution, brown.	No change.	F, darker brown.	F, slightly redder.	F, darker brown.	Unchanged.	Unchanged.	F, browner.
***Primaline, diazotised and treated with NH ₃ (cotton),	F, slightly browner; on dilution, yellow.	F, redder.	F, orange-red.	F, orange.	F, orange. S, yellowish.	Almost unchanged.	F, browner.	F, orange.
***Primaline, diazotised and treated with chloride of lime (cotton),	F and S, intense red; on dilution, yellow.	Almost unchanged.	S, browner.	Almost unchanged.	F, browner. S, yellow.	Almost unchanged.	Almost unchanged.	F, immediately an intense brown.

TABLE LXII.—GREEN DYESTUFFS.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SrCl_2 + HCl$.
Diamond green (with chromium mordanted wool).	F, blue. S, green-blue.	Brighter.	F, blue. S, pale yellow.	—	Red with green edge.	F, no action. S, —	F, no action. S, —	Little changed.
Azo-green (with chromium mordanted wool).	F, light brown. S, dirty yellow.	—	F, light brown. S, dirty yellow.	—	Yellow with orange edge.	F, nearly decolorised. S, —	F, much yellow. S, —	Much yellowed.
Dioxine (with iron-mordanted wool).	F, very dark green. S, black; on dilution, yellow.	Darker.	F, dark red-brown. S, red-brown.	—	—	F, dark brown. S, brown.	F, very dark red-brown. S, red.	—
Naphtholgreen (wool).	Dark blue-green, gradually destroyed.	No change.	Pale blue.	No change.	Dark red-brown.	Pale bluish.	Pale blue, slowly destroyed.	Decolorised.
Light green (yellowish) (wool).	F, orange. S, yellow.	Brighter.	F, orange. S, pale yellow.	—	Yellow with bright orange edge.	F, decolorised. S, —	F, decolorised. S, —	Brighter.
Light green (bluish) (wool).	F, red-brown. S, dirty yellow.	—	F, brown. S, light-brown.	—	Red-yellow.	F, decolorised. S, —	F, decolorised. S, —	—
Fast green CR (wool).	Decolorised; on washing, colour returns.	—	—	As with conc. H_2SO_4 .	As with conc. H_2SO_4 .	—	Decolorised.	Decolorised; on washing, original colour returns.
Malachitegreen(wool).	F, yellow; on dilution, green. S, red.	Lighter.	F, bright orange; on dilution, green. S, yellow.	—	Red.	F, decolorised. S, —	F, decolorised. S, —	—

Brilliant green (wool),	F, red; on dilution green. S, red.	Lighter.	F, bright yellow; on dilution, green. S, yellow.	—	Yellow-red.	F, decolorised. S, —	F, decolorised. S, —	Yellower.	
Azine green (wool),	F, dirty brown. S, —	—	F, violet. S, —	—	Brown.	—	F, darker. S, —	Brighter.	
*** Caruline (on chrome-mordanted wool),	S, dirty brown yellow; on dilution, F grey. F, lighter.	No change.	S, dirty grey.	No change.	F, lighter brown. S, yellowish.	No change.	No change.	F, red-brown. S, reddish.	
*** Neptune green SG (wool),	F, brownish yellow; on dilution, F and S green.	No change.	F, yellow; on dilution, green.	F, slightly yellower.	F, pale dirty olive-yellow; on dilution, green.	F, almost decolorised.	F, almost decolorised.	F, intense green, slowly becomes paler.	
Red Dyestuffs.									
Alizarin (with alumina-mordanted cotton) (Turkey-red),	F, little changed. S, yellowish-red; on dilution, yellow. F, dark carmine. S, dirty carmine.	No action.	F, orange to light yellow. S, light yellow.	—	Orange.	F, no action. S, —	F, violet. S, violet.	Little changed on heating, decolorised.	
Alizarin (with chrome-mordanted wool),	F, bright carmine. S, carmine.	Yellower.	F, dark red-brown. S, pale yellow.	—	Red.	F, blue-violet. S, —	F, blue-violet. S, blue.	F, on heating, light brown. S, yellow.	
Purpurine (with chrome-mordanted wool),	F, bright carmine. S, carmine.	Slightly bluer.	F, maroon. S, red.	—	Yellow with orange edge.	F, darker. S, —	F, dark purple. S, rose.	Brighter.	
Alizarin Bordeaux B (with chrome-mordanted wool),	F, deep red violet. S, deep violet.	—	F, maroon. S, dirty brown.	—	Red.	F, blue-violet. S, —	F, blue-violet. S, blue.	—	

Dye-stuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2$ + HCl.
Alizarin maroon (with chrome-mordanted wool).	F, dark cherry-red. S, deep red.	Darker.	F, darker. S, dirty brown.	—	Brownish-yellow with brown edge.	F, darker. S, —	F, darker. S, —	—
Azarine S (with aluminium-mordanted cotton).	F, magenta red; on dilution, red-dish; yellow. S, the same.	—	F, dark brown-red. S, —	—	Orange red.	F, purple. S, —	F, purple. S, red.	On heating, decolorised.
Cloth red G (wool).	F, violet. S, deep blue.	No change.	F, dark red-violet. S, light blue.	—	Dirty red with dark violet edge.	F, slightly darker. S, —	F, much darker. S, —	—
Ponceau 2G (wool).	F, much darker. S, scarlet.	No change.	F, — S, rose.	—	—	F, — S, rose.	F, orange red. S, —	—
Ponceau 2R (wool).	F, carmine. S, carmine.	No change.	F, slightly darker. S, rose.	—	Dirty yellow with pale carmine edge.	F, brighter. S, rose.	F, orange-red. S, —	Very slowly decolorised.
Biehrich scarlet (wool).	F, dark green. S, blue-green.	No change.	F, red-brown. S, —	—	Grey-blue.	F, no change. S, —	F, bluer. S, violet.	On warming, decolorised.
Croceine scarlet 3B (wool).	F, dark blue. S, deep blue.	—	F, dark blue. S, light blue.	—	Yellow with blue edge.	F, — S, rose.	F, purple. S, —	Decolorised.
Brilliant croceine M (wool).	F, violet. S, violet.	—	F, dark red-blue. S, pale blue.	—	Green-blue with dark blue edge.	F, bluer. S, —	F, purple. S, —	—
Crystal Ponceau 6R (wool).	F, deep violet. S, deep violet.	No change.	F, carmine. S, —	—	Yellow with carmine edge.	F, — S, rose.	F, brown. S, —	—

Ponceau SS extra (wool),	F, bluer. S, blue.	No change.	F, brown. S, pale blue.	—	Yellow with brown edge.	F, bluer. S, bluish-red.	F, violet. S, —	Carmine.
Fast red A (wool),	F, deep blue violet. S, violet.	No change.	F, purple. S, —	—	Yellow with dark red edge.	F, darker. S, —	F, maroon. S, —	Lighter.
Fast red E (wool),	F, dark purple. S, purple.	Brighter.	F, red maroon. S, rose.	—	Yellow with red edge.	F, darker. S, —	F, dark red-brown. S, —	Brighter.
Azo-fuchsin G (wool),	F, bluish-violet. S, violet-black.	No change.	F, brighter. S, rose.	—	Yellowish-orange.	F, bright scarlet. S, red.	F, reddish-violet. S, dirty violet.	Quickly decolorised.
Acid magenta (wool),	F, brown yellow. S, colourless; oscillation, rose.	Little change.	F, much lighter. S, rose.	—	Yellow.	F, decolorised. S, —	F, decolorised. S, —	Little changed.
Eosine (wool),	F, bright orange, becoming brown yellow. S, canary yellow.	Bright red-yellow.	F, bright red-dish-yellow. S, —	—	Yellow.	F, brighter. S, rose.	F, brighter. S, rose.	Orange yellow.
Erythrosine (wool),	F, orange-red, becoming yellow-brown. S, —	Slowly decolorised.	F, nearly decolorised. S, —	—	Yellow.	F, darker. S, rose.	F, darker, becoming orange-red. S, —	Decolorised.
Phloxine (wool)	F, bright orange, becoming brown-yellow.	Slowly decolorised.	F, yellow. S, —	—	Yellow.	F, little changed. S, rose.	F, little changed. S, rose.	Decolorised.

TABLE LXII.—RED DYE-STUFFS—continued.

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2$ + HCl.
Rose Bengale (wool), β	F, reddish-brown. S, —	Slowly de-colourised.	F, de-colourised. S, —	—	Yellow.	F, no change. S, rose.	F, darker. S, —	De-colourised.
Rhodamine B (wool),	F, yellow; colour returns on dilution. S, yellow; on dilution, rose. Orange.	Brighter.	F, orange; colour returns on dilution. S, —	—	Yellow.	F, slightly more blue. S, colourless.	F, more blue. S, colourless.	Brighter.
**Rhodamine 6G (tanned cotton),	Orange.	—	—	Orange; on washing, the original colour returns.	Orange.	—	Redder.	Unchanged.
**Rosinduline (wool),	2G Dark green.	Little change.	Brown-yellow.	Little change.	Yellow.	Little change.	Little change.	Brown.
*Chromotrope (wool),	2R Darker.	No change.	Paler.	No change.	Yellow.	More violet.	Yellowish.	Slowly lighter.
Rhodamine 6G (cotton),	F, yellow; on dilution, rose. S, yellow; on dilution, rose.	Paler.	F, orange yellow; on dilution, rose. S, —	—	F, orange. S, rose.	F, little change. S, —	F, yellow. S, light red.	Lighter.
Rhodamine S (cotton),	F, yellow; on dilution, rose. S, yellow; on dilution, rose.	Paler.	F, orange yellow; on dilution, rose. S, —	—	Orange-red.	F, little changed. S, rose.	F, paler. S, —	Lighter.

Magenta (wool and cotton),	F, darker and more blue. S, colourless.	F, yellow. S, pale yellow.	—	Yellow.	F, slowly decolorised. S, —	F, nearly decolorised. S, —	Slowly decolorised.
New magenta (wool and cotton),	F, dark maroon, becoming brown. S, colourless.	F, yellow. S, pale yellow.	—	Bright yellow.	F, slowly decolorised. S, —	F, nearly decolorised. S, —	Slowly decolorised.
Safranine (wool and cotton),	F, more blue. S, colourless.	F, dark blue. S, blue.	—	First red blue, then green, finally yellow.	F, no change. S, —	F, no change. S, —	On heating, decolorised.
* Pyronine G (cotton),	Little change.	Orange.	Little change.	Red.	Fater.	Nearly colourless.	Orange.
* Induline scarlet (cotton),	No change.	Green.	No change.	Brown-yellow.	Darker.	Darker.	Pale violet.
Congo red (cotton),	Purple.	F, deep blue. S, colourless.	—	Orange.	F, little change. S, rose.	F, little change. S, —	Decolorised.
Brilliant congo (cotton),	Purple.	F, olive-brown. S, colourless.	—	Light red.	F, no change. S, —	F, slightly yellow. S, —	Decolorised.
Benzopurpurine (cotton),	Dark purple.	F, bright blue. S, colourless.	—	Yellow.	F, little change. S, —	F, little change. S, —	Decolorised.
Dialtopurpurine (cotton),	Reddish-brown.	F, brown-olive. S, colourless.	—	Yellow.	F, no change. S, —	F, no change. S, —	Decolorised.
Diamine red (cotton),	Violet.	F, olive. S, colourless.	—	Light brown.	F, little change. S, rose.	F, little change. S, —	Decolorised.

TABLE LXII.—BROWN DYE-STUFFS

Dyestuff.	Conc. H_2SO_4 .	10 per cent. H_2SO_4 .	Conc. HCl.	10 per cent. HCl.	HNO_3 , sp. gr. 1.40.	NH_3 , sp. gr. 0.91.	10 per cent. NaOH.	$SnCl_2$ + HCl.
Dioxine (on chrome-mordanted wool),	F, dark green. S, green.	Little change.	F, darker. S, light brown.	—	—	F, dark green. S, light red.	F, very dark green. S, —	—
Fast brown (wool),	F, more blue. S, blue.	No change.	F, dark carmine. S, rose.	—	Yellow with scarlet edge.	F, darker. S, —	F, darker. S, —	—
Bismarck brown GG (wool),	F, purple; colour returns on dilution. S, red brown.	F, darker. S, colourless.	F, maroon. S, red.	—	—	F, little change. S, —	F, browner. S, —	Lighter.
Benzo brown G (cotton),	F, darker. S, grey.	No change.	F, dark brown. S, pale brown.	—	Darker.	F, little change. S, pale orange.	F, little change. S, —	Lighter.
Naphthylamine brown (wool),	F, bright blue. S, blue.	No change.	F, darker. S, blue.	—	Dirty yellow with maroon edge.	F, carmine. S, carmine.	F, bluish-red. S, colourless.	Little change.

original pattern. It is advantageous when boiling with dilute acetic acid and dilute ammonia to repeat the extraction, as a better stripping is thereby obtained, and also, with acid dyestuffs, any staining of the cotton by the first strong extract is avoided. In testing with dilute ammonia or sodium acetate, the piece is placed in a test-tube with a somewhat smaller piece of white mercerised cotton cloth, and boiled for the time prescribed. If the shade is a pale one the size of the sample should be increased and that of the cotton diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables LXIII. and LXX.), as in these cases the acid dyestuffs are less easily extracted, and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from one quarter to one minute with the hydrosulphite, then rinsed well under the tap, and allowed to lie on white paper for an hour or so. With most dyestuffs which form air-oxidisable leuco-compounds, the colour returns immediately or in a few minutes, but with others a longer time is required. The reaction is accelerated by exposing the pattern to ammonia vapour. If the colour does not return, the pattern is heated to boiling in a test-tube with a little water, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as an azo- or nitro-compound. The depth of the restored colour varies greatly in different cases; whilst with some dyestuffs the colour reappears with nearly its original depth, with others (probably on account of the greater solubility of their leuco-compounds) only a light shade may return."

The following is the general behaviour of the various groups of dyestuffs on animal fibres:—

TABLE LXIII.

Decolorised by hydrosulphite.			Not altered by hydrosulphite.	Not decolorised, but changed to brown. Original colour restored by air or persulphate.
Colour restored on exposure to air.	Colour not restored by air, but on oxidation with persulphate.	Colour not restored either by air or persulphate.		
Azines, Oxazines, Thiazines, Indigo,	Triphenylmethane group.	Nitro-, Nitroso-, and Azo-groups.	Pyrene, Acridine, Quinoline, and Thiazol groups. Some members of Anthracene group.	Most dyestuffs of the Anthracene group.

After ascertaining the dyeing group and chemical relationship of the colouring matter and taking the shade into consideration, the choice is usually considerably narrowed between a few closely related dyestuffs. These are often distinguishable by means of concentrated hydrochloric and sulphuric acid. In the appended tables (LXIV.-LXX.) the subdivision of the groups is only given in a few instances to illustrate the method.

Mixtures may be dealt with on the following lines:—When a mixture consists of two or more members of the same group it will react as a whole in a similar manner to a single member of the group, although the constituents may be differentiated in most cases by the differing rates of solution, etc.

Mixtures consisting of members of different groups will readily exhibit their differences. In many cases fractional extraction with dilute alcohol or acetic acid may be usefully employed, the separated colour being fixed on silk or wool and tested separately.

The following details refer to a few common natural colouring matters still used:—

Logwood.—This natural dyestuff is still frequently used. The chips contain very varying amounts of water. The average percentage in unfermented chips is 14 per cent. Excessive water favours fermentation. It is also sometimes treated with an alkali to give it a fictitious strength. Such logwood, if extracted with cold distilled water, will quickly affect red litmus before any of the colouring matter can be extracted.

Logwood may be tested for by extracting with alcohol and comparing the colour of the tincture with that from a standard sample.

A better method of assaying is the following:—

Some white scoured wool is mordanted by boiling in an aqueous solution of potassium bichromate containing as much of this salt as will correspond to 3 per cent. of the weight of the wool used. The mordanted wool is then introduced in small portions into a boiling bath containing the extract from a known weight of the chips or extract to be tested. As each piece takes up its full colour, a fresh portion is introduced until the bath has been exhausted, when the dyed wool is dried and weighed. The water evaporated must be replaced during the experiment.

Fibres dyed with logwood may be recognised by the following tests:—

The fabric is turned red by moderately dilute hydrochloric acid, but tannin blacks, although altered, are not reddened. If the reddened spot be pressed, while still moist, with a piece of filter paper, a red stain is produced on the paper, which turns blue if touched with a little aluminate of soda. Logwood colours are readily bleached by chlorines and hypochlorites.

If a fibre dyed with logwood be boiled with glacial acetic acid the colour is dissolved, and the solvent, when red, has a rose-red colour, changing to yellowish red on warming.

Turmeric.—The chief reaction of turmeric is that with boric acid. An alcoholic solution of the dye mixed with boric acid becomes deep red in colour. In making the test a strip of filter paper is soaked in the extract and dried at 100° C. It is then moistened with an aqueous solution of boric acid containing some hydrochloric acid, and re-dried. In the presence of turmeric a rose-red colour is produced, which is changed to purple or

Turmeric.—The chief reaction of turmeric is that with boric acid. An alcoholic solution of the dye mixed with boric acid becomes deep red in colour. In making the test a strip of filter paper is soaked in the extract and dried at 100° C. It is then moistened with an aqueous solution of boric acid containing some hydrochloric acid, and re-dried. In the presence of turmeric a rose-red colour is produced, which is changed to purple or violet-green by ammonium hydrate or soda. The red colour is reproduced by hydrochloric acid.

Turmeric should not contain more than 5 per cent. of ash, and is sometimes adulterated with starch. It may be assayed by dyeing equal weights of white woollen cloth with solutions containing equal weights of the dyes and comparing the depth of colour produced.

Brazil Wood is liable to the same adulterations as logwood, and may be examined by similar methods. Fabrics dyed with this wood are turned violet-blue by alkalis, while acids change them to yellow and red and give a pink solution. When immersed successively in hydrochloric and lime water fibres dyed red with brazil wood are changed to violet. Concentrated sulphuric acid alters brazil wood red to deep cherry-red. Peach-wood and sapan wood contain the same colouring matters as brazil wood.

Cutch should not contain more than 7 per cent. of ash and be free from starch. It also contains about 30 per cent. of catechin, which is deposited on cooling a boiling aqueous solution. Blood may be detected by treating the samples with alcohol, drying, and heating the residue in a tube, when ammonia nitrogenous vapours are evolved. Good samples give half their weight to ether.

The following table (p. 282) gives the colour reactions of fibres dyed with the more common vegetable dyes.

From 10 to 15 c.c. of each reagent is placed in a porcelain dish and a little of the leather immersed in it for from two to five minutes, after which it is taken out and washed. In the case of leather it will, as previously stated, be better to strip the colour and retransfer it to silk or wool. The reagents used are—

- | | |
|--|------------------------|
| 1. Caustic soda, | 10 per cent. solution. |
| 2. Hydrochloric acid, | } concentrated. |
| 3. Sulphuric acid, | |
| 4. Ammonium hydrate, | concentrated. |
| 5. Stannous chloride dissolved in hydrochloric acid. | |

[TABLE.

TABLE LXXI.

Colouring Matter.	Hydrochloric Acid.	Sulphuric Acid.	Caustic Soda.	Ammonium Hydrate.	Stannous Chloride and Hydrochloric Acid.	Alcohol.
Madder.	Fibre brown-red.	Fibre brownish-red, solution red.	Fibre and solution purple.	Wood brown-red.	Little colour extracted.	No action.
Archil.	Fibre little changed, solution red.	Fibre and solution purple, afterwards brown.	Fibre bluish-purple.	As with NaOH.	Fibre and solution bluish-red on heating.	Pale yellow solution.
Peach wood and brazil wood, red, Berwood.	Fibre and liquid yellowish red. No action.	Fibre yellow-red, liquid yellow. Fibre red-brown, solution dirty brown.	Fibre purple, light cherry-red. Fibre purplish, solution colourless.	Fibre purple, liquid colourless. As with NaOH.	Fibre and liquid cherry-red. Fibre unchanged, solution red.	Red solution.
Safflower.	Cotton decolorised.	Cotton decolorised.	With dil. NaOH solution pale yellow.	Cotton flesh colour.	Cotton straw-yellow.	No action.
Cochineal.	Fibre orange-red, solution orange-pink.
Old fustic.	Fibre and solution orange (or decolorised).	Fibre and solution brown (or little changed).	Fibre little changed.	Fibre unchanged, solution yellow.	Fibre orange, solution colourless.	No action.
Young fustic.	Fibre unchanged, solution pale yellow.	Fibre and solution red-brown.	Fibre red-brown.	Fibre red-brown.	No action.	No action.
Turmeric.	Fibre reddish-brown, solution colourless.	Fibre reddish-brown, solution brown.	Fibre bright reddish-brown, solution orange-brown.	Fibre bright reddish-brown, solution orange.	Fibre reddish-brown, solution colourless.	Colour extracted, solution orange or yellow with green fluorescence.
Catechu.	Fibre no change, solution pale orange.	Little or no change.	Little or no change.	Little or no change.	Fibre becomes paler, solution colourless or orange.	No action.
Logwood black.	Fibre red or olive-brown, solution deep red.	As with HCl.	Solution purple.	As with NaOH.	Fibre violet or greyish-red, solution red, afterwards brown.	No action.

CHAPTER XXII.

DISINFECTANTS AND ANTISEPTICS.

A GREAT number of disinfectants are used in the tannery for purposes other than disinfection. Thus phenol and other acids are used for delimiting. As a sterilising or pickling agent salt and sulphuric acid are largely used for foreign hides. Lime, salt, and caustic soda and potash are also employed, and sometimes direct preservatives, such as formalin; while bisulphites and sulphurous acid are of value for scouring mouldy vessels.

Examination of Salt.—*Moisture* is determined by heating to 120° C. till constant in weight.

Sodium Chloride may be estimated by titration with silver nitrate or gravimetrically (p. 58).

Insoluble Matter.—A weighed quantity (5 grms.) is dissolved in distilled water and the solution filtered into a 250 c.c. flask, the undissolved residue of sand, etc., being dried, ignited, and weighed. Fifty c.c. of the filtrate are then treated with ammonia and ammonium chloride and the iron and aluminium oxides filtered off and weighed. Lime and magnesia are estimated in the filtrate in the same way as in a water residue. Sulphates should also be determined and calculated to sodium sulphate. The following are examples by commercial salts (No. 5 is a recovered salt):—

	1	2	3	4	5
Sodium sulphate, . . .	1.14	0.05	1.39	1.03	17.46
Sodium chloride, . . .	97.20	97.52	92.26	98.68	64.38

BI-SULPHITES AND SULPHUROUS ACID (see p. 38).

Phenol, and similar disinfectants, as carbolic acid, may be estimated by the process given on page 39.

Formaldehyde.—This is sold chiefly under the name of formalin, a 40 per cent. aqueous solution of the aldehyde. In fairly pure solutions the strength may be approximately determined from the specific gravity. The following figures are given by Davis (*J.S.C.I.*, 1897, 502):—

TABLE LXXIV.

Sp. gr. at 15.5° C.	Percentage of Formaldehyde by weight.	Percentage of Formaldehyde by volume.
10,025	1.0	1.0
10,125	5.0	5.0
10,250	10.0	10.25
10,380	15.0	15.60
10,530	20.0	21.1
10,670	25.0	26.7
10,830	30.0	32.5
11,040	35.0	38.6
11,250	40.0	45.0

Formalin may be determined by heating 5 c.c. with 50 c.c. of normal ammonium hydrate solution in a closed bottle to a temperature of 50° C., or letting the mixture stand at ordinary laboratory temperatures for some hours.

The ammonia and formaldehyde combine, giving formaldehyde-ammonia. After the reaction is complete the excess of unused ammonia is titrated with normal acid and cochineal. The number of cubic centimetres of normal ammonia used multiplied by 9 gives the percentage of formalin.

C. Wällnitz (*Analyst*, 1903, p. 189) recommends the following methods as the most reliable. They are:—

(1) *Blank and Finkenbeiner's Method*.—Three grms. of the solution or 1 gm. of a solid preparation are placed in a tall flask with 25 c.c. of 2N sodium hydrate solution. Fifty c.c. of 2.5 or 3 per cent. pure hydrogen peroxide are then slowly added. After standing for half an hour the alkali is titrated with 2N sulphuric acid and litmus. In the case of formalins stronger than 45 per cent., 30 c.c. of sodium hydrate should be used. The volume of standard alkali used multiplied by 6 gives the formaldehyde in 1 gm. of the solid, or, multiplied by 3, in 3 grms. of the solution.

(2) *Romijn's Method*.—Ten c.c. of the aldehyde solution are mixed with 25 c.c. of decinormal iodine solution, and sodium hydrate added drop by drop until the liquid becomes clear and yellow. After 10 minutes sufficient hydrochloric acid is added to liberate the uncombined iodine, which is then determined by titration with decinormal thiosulphate solution. Two atoms of iodine are equivalent to 1 molecule of formalin. About 70 c.c. of iodine solution are required for every 5 c.c. of 2 per cent. formalin solution.

GLOSSARY OF TECHNICAL TERMS USED IN THE TANNING INDUSTRY.

- Antiseptics.**—Bodies which temporarily check fermentation, such as dilute solution of *formaldehyde, salt, etc.*
- Bating.**—The treatment of skins with an infusion of hen or pigeon dung in order to neutralise lime and render them flaccid. Bating also opens the pores of the skin and thus assists subsequent processes.
- Buffing.**—The removal of the grain of leather by mechanical means to remove defect and obtain a level surface.
- Butt.**—The square part of the hide, the best part of the skin.
- Chamois.**—Leather produced by the incorporation of an oxidisable oil, such as cod oil. After incorporation of the oil the skins are allowed to ferment, when oxidation takes place, accompanied by the production of heat; the skin is converted into a leather which, while being extremely supple, is enduring and impermeable.
- Currying.**—The treatment of skins (generally lightly tanned) with oil to render them *enduring and supple.*
- Deliming.**—The soaking of skins after liming in a weak acid solution to dissolve out lime.
- Depilation.**—The process following the soaking of hides. It consists in immersing the skin in an infusion of lime or other substance which loosens the hair without damaging the skin.
- Disinfectants.**—Bodies which kill both bacteria and their spores.
- Drench.**—A mixture of bran and water which has been allowed to ferment, thus containing, among other things, acetic and lactic acids. It neutralises an removee lime, and has a plumping effect.
- Fat Liquor.**—An emulsion of soap and oil and a mild alkali, such as borax, in which skins are worked after tanning and washing.
- Fleshing.**—The removal with a knife of portions of flesh, etc. which adhere to the hide. Fleshings contain considerable quantities of fat and gelatine which are recovered.
- Hides (Green).**—*Raw hides from the butchers.*
- Hides (Split).**—A hide that is split into two layers. The grain layer is used for good and the lower for commoner leather.
- Hip.**—A tanned split skin, of a weight between a calf and a light hide, also sometimes raw calf skin or partially tanned East Indian hide.
- Pelts.**—Skins as received by the tanner without hair.

Plumping.—The softening and swelling of skin fibres which contain little water. Plumping follows upon the removal of salt on treatment with dilute acids and alkalis.

Puering.—The same as bating, except that dog dung is used.

Salted or Pickled Hides.—Those which have been cured with an antiseptic. Salt and sulphuric acid are used largely for this purpose; but other preparations, such as lime and caustic alkalis, are also employed. Formaldehyde and other organic disinfectants are sometimes used.

Skiver.—The grain side of a split sheepskin tanned with sumach.

Soaking.—The washing of hides with water to remove dirt or salt previous to liming.

Sweating.—A natural process of putrefaction brought about by storing hides in a warm and damp atmosphere with the object of encouraging the growth of bacteria that will loosen hair.

Tanning.—The treatment of prepared skins with infusions containing a form of tannic acid in order to render the skin fibre insoluble and permanent.

Tawing.—The treatment of skins with compounds of chromium, aluminium, etc.

Trimnings.—The useless parts of a hide which are used for glue manufacture.

Unhairing.—The mechanical removing of the loosened hair after the action of the depilatory.

INDEX.

- ACETIC acid, determination of, 68.
separation of, from formic acid, 73.
- Allen and Searle, determination of gelatin, 246.
- Alkalis, analysis of, 59.
estimation of, in water, 42.
- Alum, analysis of, 169.
- Alumina, estimation of, 40.
use of, in analysis of tanning materials, 133.
- Ammonia, determination of, 58.
in water, 27.
- American official method for tanning materials, 136.
- American shake method, 128.
- Andreasch, analysis of sumach, 156.
- Antiseptics, *Gloss.*, 285.
- Appelius and Schüll, analysis of chrome liquors, 174.
- Archbutt, Maumené test, 194.
viscometer, 242.
- Arsenic, determination of, 51.
- Arsenic sulphide, analysis of, 61.
- BALDRACCO, analysis of dégras, 202.
- Bartel, determination of hide substance, 226.
- Barium, estimation of, in leather, 227.
- Bating, *Gloss.*, 285.
- Becker, detection of iron in sumach, 163.
- Bell filter, 120.
criticisms of, 126.
- Bennett, hide powder for chroming, 150.
- Benzine for degreasing, 250.
- Benzine, distillation test, 252.
- Bloom, measurement of, 166.
- Boric acid, estimation of, 74.
- Brazil wood, 281.
- Bromide value, 195.
- Buffing, *Gloss.*, 285.
- Butt, *Gloss.*, 285.
- CALN and Thorpe, synthetic dyestuffs, 257.
tables of dyestuffs, 262.
- Caloric power, determination of, 1.
- Calorimeter, 2.
- Candle filter, 117.
- Carbolic acid, estimation of, 76.
- Carbon dioxide, estimation of, 57.
- Carnauba wax, 200.
- Catechin, 98.
- Catechol, 98.
- Caven and Hill, determination of glucose, 231.
- Chamois, *Gloss.*, 285.
- Chestnut, 168.
- Chlorides, estimation of, 21.
- Choudrin, 249.
- Chromates and chromium salts, analysis of, 170.
- Chromed hide powder method, 136.
- Chromic oxide, determination of, in leather, 227.
- Collin solution, preparation of, 129.
- Colour measurement, 152.
of water, 20.
weight, 132.
- Crouzel, estimation of tannic acid, 105.
- Currying, *Gloss.*, 285.
- Cutch, 281.
- DÉGRAS, 201.
- Degreasing agents, 250.
- Deliming, *Gloss.*, 285.
- Depilation, 54; *Gloss.*, 285.
- Disinfectants, 283.
- Dodge, determination of tannic acid, 133.
- Dreher, estimation of chromic acid, 172.
- Drenches, *Gloss.*, 285; analysis of, 77.
- Dumas, determination of nitrogen, 4.
- Dyestuffs, analysis of, 257.
classification of, 256.
fastness of, 260.
identification of, 260-280.
reactions of mixtures, 280.
vegetable, 280-282.
- EARP, bell filter, 121.
specific gravity of leather, 232.
- Effluents, analysis of, 45.
- Egg yolk, 204.
- Eitner, analysis of lime liquors, 63.
- Ellagic acid, 99.
- FAT LIQUOR, *Gloss.*, 285.
- Fat liquors, 204.
- Fatty acids, determination of, 190.
oxidised, 193.
volatile, 192.
titer of, 213.
- Fibre, determination of, 79.
- Filtration of tanning extracts, 116.
- Fleshings, *Gloss.*, 285; analysis of, 237.
- Formaldehyde, analysis of, 283.

- Formalin gelatin, 185.
hide powder, 186.
Formic acid, 68, 70-73.
- GALLIC acid, 98.
determination of, 104.
Gambier, 167.
Gases in effluents, 45.
Gelatin, determination of, 245.
precipitation of, with zinc sulphate, 247.
Georgievic, analysis of dyestuffs, 258.
Glue, 238.
analysis of, 244.
determination of gelatin in, 245.
peptones, 248.
foaming of, 243.
physical tests for, 239.
viscosity of, 241.
Glycerin, analysis of, 207.
determination of, in soap, 214.
Godfrin, extractor for leather, 225.
Goutal, determination of calorific power, 1.
Green, determination of dyestuffs, 261.
- HARDNESS in water, determination of, 32.
Helmer and Mitchell, hexabromide value, 195.
Hide powder for chroming, 150.
method of analysis, 108.
preparation and properties of, 124.
Hides substance, estimation of, 226.
Hides, *Gloss.*, 285, 286.
Hoppenstedt, analysis of tanning materials, 133.
determination of acidity in liquors, 179.
Hübl, iodine solution, 192.
Hydrochloric acid, estimation of, 70.
normal solution, 12.
Hydrostatic balance, 183.
- INDICATORS, 14.
International method of tanning analysis, 146.
Iodine value, determination of, 190.
Iron, estimation of, 40.
- JAPAN wax, 200.
Jean, analysis of dégras, 202.
sulphides, 62.
determination of gelatin, 246.
estimation of tannic acid, 104.
- KIP, *Gloss.*, 285.
Kissling, test for glue, 240.
Kjeldahl, method of determining nitrogen, 5.
Koch, extractor, 113.
Kopecky, analysis of chrome liquors, 178.
method of tanning analysis, 143.
- LACTIC acid, 68.
analysis of, 73.
Lamb, determination of mineral acid in leather, 234.
microscopic examination of sumach, 159.
Lead, estimation of, in leather, 227.
- Leather, determination of chromic oxide in, 227.
hide substance, 226.
mineral acid in, 233.
mineral constituents, 227.
soluble matter in, 225.
specific gravity of, 232.
sugar in, 229.
sulphur in, 235.
Lepetit, analysis of quebracho, 166.
Levi, analysis of sodium thiosulphate, 175.
Lewkowitzsch, specific gravity of oils, 184.
phytosterol acetate test, 194.
titer test, 213.
Lime, analysis of, 54.
estimation of, 40.
liquors, analysis of, 63.
Lipowitz, strength test for glue, 239.
Logwood, 282.
Lovibond, tintometer, 153.
Löwenthal, method of determining tannic acid, 106.
- MAGNESIA, estimation of, 40.
Mangrove, 167.
Mardick, analysis of tanning materials, 133.
Maumené test, 196.
Methylated spirit, rectification of, 189.
Mennier, determination of sulphuric acid in leather, 236.
Microtome, 221.
Mineral tannages, 169.
Myrobalans, 164.
- NESSLER solution, 26.
Nierenstein, analysis of sumach, 158.
Nihoul, conditions affecting solubility of tannin, 122.
determination of nitrogen, 7.
selection of water supply, 16.
Nitrates, estimation of, 23.
Nitric acid, estimation of, 69.
Nitrogen, determination of, 4.
- OAK bark, 168.
O'Callaghan and Randall, analysis of sumach, 158.
- Oil, cod, 196.
fish, 197.
linseed, 199.
menhaden, 196.
neetsfoot, 198.
olive, 198.
seal, 197.
shark, 197.
turkey red, 199.
whale, 197.
- Oils, analysis of, 181.
insoluble matter in, 182.
sampling of, 181.
Oxalic acid, estimation of, 68.
normal solution, 12.
Oxygen absorbed by water, determination of, 29.

- PARSSLEE**, method of analysis for tanning materials, 142.
Palmer, method of analysis for detannising, 128.
Parker and Blockley's composition of myrobalans, 164.
 estimation of weight-giving power of tanning materials, 151.
Parker and Cassburi, determination of soluble leather, 179.
Parker and Leech, composition of valonia, 165.
Parker and Payne, candle filter, 117.
 collin method of detannising, 129.
 determination of sulphuric acid in liquors, 178.
 determination of tannic acid, 105.
Pelts, *Gloss.*, 286.
Permanganate solution, Wanklyn, 27.
Pfeifer, determination of hardness, 35.
Philip, analysis of lactic acid, 74.
Phlobaphenes, 99.
Phloroglucin, 98.
Phosphates, determination of in dung, 80.
 in water, 86.
Pistacia, 164.
Plumping, *Gloss.*, 286.
Potassium bichromate, decinormal solution, 14.
 hydrate, normal solution, 12.
 permanganate, decinormal solution, 14.
Priestman, microscopic examination of sumach, 161.
Procter, analysis of lime liquors, 64.
 bell filter, 120.
 determination of acidity in liquors, 177.
 determination of hardness, 34.
 recognition of tannins, 82.
Procter and Bennett, bromide value, 195.
Procter and Blockley, absorption of non-tannins by chromed powder, 141.
 correction for filter papers, 117.
Procter and Heal, estimation of chromic acid, 172.
Procter and M'Canllich, analysis of chrome liquors, 174.
Procter and Searle, determination of mineral acid in leather, 233.
Protocatechic acid, 99.
Puering, *Gloss.*, 286.
Pyrogallol, 98.

QUEBRACHO, 166.
 extract, 167.

REFRACTIVE INDEX, determination of, 185.
Refractometer, 185.
Richards and Palmer, estimation of tannic acid, 103.
Rideal, strength of glue jelly, 240.
Rideal and Stewart, determination of gelatin, 246.
Rosenhain, calorimeter, 2.

SALT, analysis of, 285.
Sand filter extractor, 111.
 Saponification equivalent, 190.
 Searlata, analysis of sumach, 159.
 Scutch, analysis of, 237.
 Shake method, 128.
 Silver nitrate, decinormal solution, 13.
 Skin, analysis of, 222.
 preparation of sections, 219.
 structure of, 217.
 Skin grease, 206.
 Skiver, *Gloss.*, 286.
 Soaking, *Gloss.*, 286.
 Soap, analysis of, 210.
 resin in, 212.
 Sodium carbonate, analysis of, 60.
 carbonate, normal solution, 11.
 hydrate, analysis of, 60.
 hydrate normal solution, 12.
 sulphate, analysis of, 61.
 thiosulphate, analysis of, 175.
 decinormal solution, 13.
 resin in, 212.
 Soluble leather, determination of, 179.
 non-tannins, determination of, 120.
 Sprenzel tube, 184.
 Standard solution, 11.
 Starch solution, 13.
 determination of, 78.
 Steaming, analysing of chrome liquors, 174.
 Sugar, determination of, 229.
 Sulphates, estimation of, 43.
 Sulphuric acid, analysis of, 71.
 normal solution, 11.
 Sulphurous acid, analysis of, 76.
 Sumach, characters and analysis of, 155.
 Sweating, *Gloss.*, 286.

TALLOW, 199.
Tamarix, 164.
Tannic acid, 99.
 estimation of, 103.
Tanning, *Gloss.*, 286.
Tanning analysis, international method of, 146.
 materials, analysis of, 108.
Tannins, qualitative tests for, 82.
Taxing, *Gloss.*, 286.
Thermostat, 187.
Thompson, estimation of tannic acid, 104.
Tintometer, 183.
Titanium, estimation of, 228.
Titre test for fatty acids, 213.
Total solids in water, 19.
 soluble matter, determination of, 119.
Trimings, *Gloss.*, 286.
Trotman, distillation of benzene, 252.
 estimation of arsenic, 51.
 of nitrates in water, 23.
 mineral constituents of sumach, 162.
Trotman and Hackford, detannisation of liquors, 124.
 determination of gelatin, 247.
 tannic acid, 105-132.
 effect of peptones in glue, 247.
 extraction of tanning materials, 115.
 foaming in glue, 243.
 laboratory heater, 189.

- Turnbull, mineral constituents of sumach, 164.
 solubility of hide powder, 123.
 Turmeric, 281.
- UNHAIRING, *Gl'oss.*, 286.
- Unsaponifiable matter, determination of, 188.
- VARNISHES, 215.
- Vaubel, determination of tannic acid, 135.
- Veitch extractor, 113.
- Viscometer, 242.
- Volatile fatty acids, determination of, 192.
- WANKLYN, method of water analysis, 26.
- Water, analysis of, 18.
 calculation of results of analysis, 43
influence of purity of, on extraction of tanning materials, 15-18
- Water, standards, 37.
- Waxes, 200.
- Weight-giving properties of tanning materials, 151.
- Weiss, extractor, 113.
 method of tanning analysis, 143.
- Wenkibelech, gelatinisation of glue, 239.
- Wigs, *iodine solution*, 191.
- Wislicenus, analysis of tanning materials, 133.
- Wolff, colorimeter, 258.
- Wood, composition of dung, 81.
 vapour tension of benzine, 253.
- Wood and Holmes, use of box calf shavings, 143.
- Wood and Wilcox, analysis of drenches, 77.
 composition of bran, 78.
- ZEISS, refractometer, 185.

**CHARLES GRIFFIN & COMPANY,
LIMITED.**

**A SELECTION FROM
CHARLES GRIFFIN & CO.'S PUBLICATIONS.**

SCIENTIFIC AND TECHNICAL WORKS.



MESSRS. CHARLES GRIFFIN & COMPANY'S PUBLICATIONS may be obtained through any Bookseller in the United Kingdom, or will be sent on receipt of a remittance to cover published price and postage. To prevent delay, Orders should be accompanied by a Cheque or Postal Order crossed "UNION OF LONDON AND SMITH'S BANK, Chancery Lane Branch."

Telephone—
1634 City.

LONDON:

Telegrams—
Explanatus.

12 EXETER STREET, STRAND.

W.T. 64. G.xii.

	PAGE		PAGE
ADAMS (W. P.), Motor Car Mechanism, -	22	LAFAR, Technical Mycology, -	48
ALLEN (T.), Road Making, -	45	LAMBERT, Glee, Gelatine, &c., -	67
ALFORD (C. J.), Mining Law, -	42	LARARD (C. E.), Eng. Calculations, -	26
ALLINGHAM (A.), Metallurgy, -	64	LAW (E. F.), Alloys, -	42
ANGLIN (S.), Design of Structures, -	15	LAWN (J. G.), Mine Accounts, -	42
ARCHBUTT & DEKLEY, Lubrication, -	21	LEEDS (F. H.), Acetylene, -	63
ASKING & ROESSLER, Internal Com- bustion Engines, -	23	LEVY (D. M.), Copper Smelting, -	51
ATHERTON (Wm.), Design of Boams, -	12	LIECKFELD (G.), Oil Motors, -	52
BARKER (D. W.), Works by, -	35	LIVERIDGE, Engin. Room Fracitor, -	20
BERINGER (J. J. & C.), Assaying, -	61	MACKENZIE (T.), Mechanics, -	36
BICHEL & L'ARSEN, Explosives, -	43	MACLEOD and WALKER, Met. Chem., -	51
BILES (Prof.), Construction of Ships, -	64	MCABEN (B. S.), Elem. Mech. Eng., -	26
BJORLING (P. H.), Pest, -	61	McMILLAN (R. A.), Marine Eng. Calc., -	19
BLOUNT & BLOXAM, Chemistry, -	56	— & ROCHERS Electric Smelting, -	53
BLYTH (A. Wynter), Foods and Poisons, -	67	McWILLIAM, Foundry Practice, -	54
BOHLE, Elect. Photometry, -	22	MASSEY ON, Celluloid, -	60
BOHLE & ROBERTSON, Transformers, -	30	MENNUM (S.), Hydrographic Surveying, -	44
BOCHERS (Dr.), Electric Smelting, -	53	MIDDLETON (R. E.), Water Supply, -	64
BROUGH (B. H.), Mine Surveying, -	41	MILL (Dr. R. H.), New Lands, -	47
BRUCE (R.), Food Supply, -	43	MILLAR (W. J.), Latitudes & Longitude, -	35
BROCK (H. C.), Algebra & Trigonometry, -	36	MITCHELL (C. A.), Fresh Foods, -	57
BURNS (L.), Colliery Electricity, -	42	— & HEPWORTH (T. C.), Loco., -	65
BUTLER, Works by, -	17, 22	MORGAN (J. J.), Works by, -	21, 54
BUTTERFIELD, (W. J. A.), Gas, -	66	MUNRO & JAMIESON'S Elec. Pkt.-bk., -	34
CADMAN & BALDANE, Air of Mines, -	39	MUNRO (R. D.), Works by, -	21
CALIN & THORPE, Synthetic Dyes, &c., -	68	NAYLOR (W.), Trades Waste, -	62
CARTER (H. L.), Long Fibre Spinning, -	69	NICHOLSON (W.), Smoke Abatement, -	63
CASTELL-EVANS, Chemical Tables, -	36	NORMANDY (F.), Sea Water Distillation, -	20
CHATLEY (H.), Works by, -	24, 33	NORTH (S.), Oil Fuel, -	65
COLE (Prof. G. A. J.), Works by, -	46, 73	OPPENHEIMER (C.), Works by, -	59
COLE (W. H.), Light Railways, -	21	PARR (J.), Works by, -	41, 44
COLLINS (H. F.), Lead and Silver, -	49	PEARCE (W. J.), Painting, -	66
COSTE (J. H.), Caloric Power of Gas, -	63	PETTORROW (W. F.), Loco. Eng., -	21
COX (S. H.), Prospecting or Minerals, -	45	PHIPSON (Dr. T. L.), Earth's Atmosphere, -	47
CRAWFORD (W. J.), Graphic Statics, -	31	POISCHL (V.), Chemistry of Colloids, -	62
CRITCH (A.), Telegraph Systems, -	69	POYNTING (J. H.), Mean Density, -	74
CUNNINGHAM, Docks and Harbours, -	16	— & THOMSON, Physic., -	74
DAVEY (H.), Pumping Machinery, -	17	PRAEGER (H. L.), Open Air Botany, -	73
DAVIS (J. R.), Works by, -	71, 91, 92	PUPPE (J.), Rolling Mills, -	24
DIXON (G.), Bird Life, -	23	RAND METALLURGICAL PRACTICE, -	52
DONKIN (Bryan), Works, -	22, 23	RANKINE'S Works, -	29
DUERR (Geo.), Bleaching, &c., -	70	RAWSON, GARDNER, & LAYCOCK, Dictionary of Dyestuffs, -	68
DUNBAR (Prof.), Sewage Treatment, -	62	REDGRAVE (G. H.), Cements, -	67
DUPRE & HARR, Manual of Chemistry, -	70	REDWOOD (Sir Boverly), Petroleum, -	52
EICHORN, Wireless Telegraphy, -	30	— & THOMSON, Handbook, Petroleum, -	52
ETHELIDGE (H.), Geology, -	46	REID (Geo., M. D.), Sanitation, -	64
FARNSWORTH, Cons. Steel Work, -	15	REICHMOND (H. D.), Works by, -	58
FARRELL (F. J.), Dyeing and Clearing, -	79	RIEMER (J.), Shaft Sinking, -	42
FIDLER (Prof.), Bridge Construction, -	16	ROBERTS-AUSTEN, Metallurgy, -	42
FIELD (E. R.), Mining Report Book, -	42	ROBINSON (Prof.), Hydraulics, -	47
FOSTER (Sir C. Le Neve), Works by, -	39	ROSE (T. L.), Gold Metallurgy of, -	48
GAIRNS (J. F.), Loco. Compounding, -	21	ROTHWELL (O. F. S.), Textile Printing, -	70
GATHOUSE (F.), Cement Handbook, -	62	SCHWARTZ (Dr. von), Fire Risks, -	83
GAUSBURG (Dr.), Submarine's Duties, -	37	SEARLE (A. B.), Works by, -	19
GISSING (F. T.), Pest, -	61	SEATON (L. E.), Works by, -	61
GOLDING (H. A.), Works by, -	26	SEXTON (Prof.), Works by, -	52, 71
GROSSMANN (J.), Chem. Engineering, -	70	SHOWELL (P. G.), Navigation Deductions, -	58
GRUNWALD (L.), Enamelling on Metals, -	65	SINDALL, Paper Technology, -	60
GROVER (G.), Metallic Alloys, -	53	SMITH (C. A.), Suction Gas Plants, -	90
GURDEN (R.), Traverse Tables, -	26	SMITH (C. W.), Dustless Roads, -	23
GUTTMANN (O.), Blasting, -	43	SMITH (Prof. R. H.), Works by, -	27
HALDANE (G. S.), Air Analysis, -	39	SMITH (W.), Shipmaster's Medical Help, -	37
HALSE (E.), Spanish Mining Terms, -	42	SOLOMON (H. G.), Electricity Meters, -	61
HANNAN (W. L.), Textile Fibres, -	39	SOLOMON, Ceramic Literature, -	61
HARBOLD & HALL, Steel, -	54	SORBY (Lt.-Col.), Geology for Engineers, -	46
HARRISON (J. W.), Sanitation, -	60	STEWART (R. W.), Elementary Physics, -	74
HATFIELD (W. L.), Cast Iron, -	51	STOCKS (H. B.), Water Analysis, -	60
HEIL & ESCH, Rubber Goods, -	67	STRICKLAND (F.), Petrol Motors, -	69
HEWLETT (G.), Diet. Sea Terms, -	38	SUPLICE (H. H.), Works by, -	23, 27
HEVLIN (H.), Cot. Weavers' Handbook, -	63	SWYKS (Dr. H. J.), Browling, -	59
HIGGS (J. A.), Mineral Oil Testing, -	58	TAYLOR (F. N.), Works by, -	18
HILL (G.), Electric Crane Construction, -	30	TRAILL (T. W.), Boilers, -	67, 69
HOBS (L.), Engine Design, -	18	TROTMAN (S. K.), Works by, -	31
HOERNES (Lieut.-Col.), Aviation, -	32	TUNZELMANN (G.), Electrical Theory, -	31
HUGHES (H. W.), Coal Mining, -	40	TURNER (Thos.), Works by, -	50, 52, 54
HUGHES (H. W.), Works by, -	28	WALTON (T.), Works by, -	84
HURST (Chas.), Works by, -	25	WANG (C. Y.), Works by, -	46, 60
HURST (G. H.), Works by, -	66	WEBER (Dr. C. O.), India Rubber, -	67
INGLE (H.), Agricultural Chemistry, -	56	WELLS (S. H.), Engineering Drawing, -	26
JACOPER (J. E.), Mechanical Drawing, -	25	WILEY (T. E.), Jeweller's Art, -	54
JAMIESON (Prof.), Castles, -	14	WILLOUGHBY (Dr. E. F.), Milk, -	58
JOHNSON (J. C. F.), Getting Gold, -	44	WILKES (W. H.), Shipmasters' Duties, -	64
JORGENSEN (A.), Micro-Organisms, -	58	WOOD (Francis), Sanitary Engineering, -	28
JUDE (A.), Steam Turbine, -	20	WORDINGHAM, Electrical Stations, -	3
JULIAN & SMART, Crystallizing, -	44	WORDINGHAM, Oils and Fats, -	6
KASSNER (T.), Gold Seeking, -	14	YULE (G. U.), Theory of Statistics, -	76
KERR (G. L.), Works by, -	46	ZIEMER (G.), Works by, -	66
KESHAW (G. E.), Sewage Disposal, -	62		
KNECHT, Works by, -	68, 69		

FIFTH EDITION, Revised. In Large 8vo. Pp. i-xxiv + 511. With 255 Diagrams, Examples, and Tables, and a Chapter on Foundations. Cloth, 16s.

THE DESIGN OF STRUCTURES:

A Practical Treatise on the Building of Bridges, Roofs, &c.

BY S. ANGLIN, C.E.,

Master of Engineering, Royal University of Ireland, late Whitworth Scholar, &c.

"We can unhesitatingly recommend this work not only to the Student, as the **BEST TEXT-BOOK** on the subject, but also to the professional engineer as an **EXCEEDINGLY VALUABLE** book of reference."—*Mechanical World*.

In Large Crown 8vo. Cloth. Pp. i-xiv + 236. With 201 Illustrations. 6s. net.

AN INTRODUCTION TO

THE DESIGN OF BEAMS, GIRDERS, AND COLUMNS

IN MACHINES AND STRUCTURES.

With Examples in Graphic Statics.

BY WILLIAM H. ATHERTON, M.Sc., M.I.MECH.E.

"A very useful source of information. . . . A work which we commend very highly."—*Nature*.

FOURTH EDITION, Thoroughly Revised. Royal 8vo. Pp. i-xxx + 456. With 239 Illustrations in the Text, and 13 Lithographic Plates. Handsome Cloth. Price 30s.

A PRACTICAL TREATISE ON BRIDGE-CONSTRUCTION:

Being a Text-Book on the Construction of Bridges in Iron and Steel.

FOR THE USE OF STUDENTS, DRAUGHTSMEN, AND ENGINEERS.

BY T. CLAXTON FIDLER, M. INST. C. E.,

Late Prof. of Engineering, University College, Dundee

"The new edition of Mr. Fidler's work will again occupy the same **CONSPICUOUS POSITION** among professional text-books and treatises as has been accorded to its predecessors. **SOUND, SIMPLE, AND FULL.**"—*The Engineer*.

In Medium 8vo. Pp. i-xv + 248. With 103 Illustrations. Price 10s. 6d. net.

CONSTRUCTIONAL STEELWORK:

Being Notes on the Practical Aspect and the Principles of Design, together with an Account of the Present Methods and Tools of Manufacture.

BY A. W. FARNSWORTH,

Associate Member of the Institute of Mechanical Engineers.

A worthy volume, which will be found of much assistance. . . . A book of particular value."—*Practical Engineer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION, Revised. In Large 8vo. Handsome Cloth, Gilt.
With 37 Folding Plates and nearly 500 Illustrations in
the Text. 30s. net.

The Principles and Practice of **DOCK ENGINEERING.**

By BRYSSON CUNNINGHAM.

GENERAL CONTENTS.

Historical and Discursive.—Dock Design.—Constructive Appliances —
Materials.—Dock and Quay Walls.—Entrance Passages and Locks.—
Jetties, Wharves, and Piers.—Dock Gates and Caissons.—Transit Sheds
and Warehouses.—Dock Bridges.—Graving and Repairing Docks.—
Working Equipment of Docks.—INDEX.

"We have never seen a more profusely-illustrated treatise. It is a most important
standard work, and should be in the hands of all dock and harbour engineers."—*Steamship*.
"Will be of the greatest service to the expert as a book of reference."—*Engineer*.

In Large 8vo. Pp. i-xii + 233. With 18 Plates, 11 Tables, and 220
Illustrations in the Text. 16s. net.

A COMPANION VOLUME TO "DOCK ENGINEERING."

THE PRINCIPLES AND PRACTICE OF **HARBOUR ENGINEERING.**

By BRYSSON CUNNINGHAM.

CONTENTS.—Introductory.—Harbour Design.—Surveying, Marine and
Submarine.—Piling.—Stone, Natural and Artificial.—Breakwater Design.—
Breakwater Construction.—Pierheads, Quays, and Landing Stages.—
Entrance Channels.—Channel Demarcation.—INDEX.

"The best and most complete book we have seen on the subject."—*Steamship*.
"This is a standard work . . . sure to prove a valuable book of reference."—
Shipping World.

In Crown 8vo. Handsome Cloth. Pp. i-xiv + 504. With many Illus-
trations, including 7 Coloured and 15 Other Plates. 12s. net.

HYDROGRAPHIC SURVEYING.

For the Use of Beginners, Amateurs, and Port and
Harbour Masters.

By COMMANDER S. MESSUM, R.N.,

Instructor in Nautical Surveying, R.N. College, Greenwich.

CONTENTS.—Sextant.—Protractor.—Station Pointer.—Theodolite.—Projections.—
Symbols and Abbreviations.—Plotting and Triangulation of a Small Plan.—Mast-head
Angle Survey.—Meridian Distances.—APPENDIX.—INDEX.

"Eminently practical from beginning to end."—*Engineer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

THIRD EDITION, *Thoroughly Revised and Enlarged.* Pp. i-xvi+227.
With 60 Plates and 71 other Illustrations. Handsome Cloth. 25s. net.

HYDRAULIC POWER AND HYDRAULIC MACHINERY.

By HENRY ROBINSON, M.Inst.C.E., F.G.S.,

FELLOW OF KING'S COLLEGE, LONDON; PROF. EMERITUS OF CIVIL ENGINEERING,
KING'S COLLEGE, ETC., ETC.

CONTENTS—Discharge through Orifices.—Flow of Water through Pipes.—Accumulators.—Presses and Lifts.—Hoists.—Rams.—Hydraulic Engines.—Pumping Engines.—Capstans.—Traversers.—Jacks.—Weighing Machines.—Riveters and Shop Tools.—Punching, Shearing, and Flanging Machines.—Cranes.—Coal Discharging Machines.—Drills and Cutters.—Pile Drivers, Excavators, &c.—Hydraulic Machinery applied to Bridges, Dock Gates, Wheels and Turbines.—Shields.—Various Installations.—Meters.—INDEX.

"The standard work on the application of water power."—*Cassier's Magazine.*

Second Edition, *Greatly Enlarged.* Pp. i-xiv+336. With Frontispiece,
12 Plates, and 279 other Illustrations. 21s. net.

THE PRINCIPLES AND CONSTRUCTION OF PUMPING MACHINERY (STEAM AND WATER PRESSURE).

With Practical Illustrations of ENGINES and PUMPS applied to MINING,
TOWN WATER SUPPLY, DRAINAGE of Lands, &c., also Economy
and Efficiency Trials of Pumping Machinery.

By HENRY DAVEY, M.Inst.C.E., M.Inst.Mech.E., &c.

CONTENTS—Early History of Pumping Engines—Steam Pumping Engines—Pumps and Pump Valves—General Principles of Non-Rotative Pumping Engines—The Cornish Engine, Simple and Compound—Types of Mining Engines—Pit Work—Shaft Sinking—Hydraulic Transmission of Power in Mines—Electric Transmission of Power—Valve Gears of Pumping Engines—Water Pressure Pumping Engines—Water Works Engines—Pumping Engine Economy and Trials of Pumping Machinery—Centrifugal and other Low-Lift Pumps—Hydraulic Rams, Pumping Mains, &c.—INDEX.

"By the 'one English Engineer who probably knows more about Pumping Machinery than any other.' . . . A VOLUME RECORDING THE RESULTS OF LONG EXPERIENCE AND STUDY."—*The Engineer.*

In Medium 8vo. Cloth. With about 300 Illustrations.

MODERN PUMPING AND HYDRAULIC MACHINERY.

By EDWARD BUTLER, M.I.Mech.E.

(Author of "Carburettors, Vaporisers, and Distributing Valves.")

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Medium Svo. With over 1000 Illustrations. Cloth. 25s. net.

A MANUAL OF CIVIL ENGINEERING PRACTICE,

Specially Arranged for the Use of Municipal and County Engineers.

By F. NOEL TAYLOR, CIVIL ENGINEER.

CONTENTS.—Ordnance Maps.—Chain surveying.—Surveying with Angular Instruments.—Leveling.—Adjustment of Instruments.—Measurement of Areas, Volumes, &c.—The Mechanics of Engineering, &c.—Beams.—Pillars, Stanchions and Shafting.—Design of Structures. Arches.—Graphic Statics.—Materials of Construction.—Engineering Foundations.—Brickwork and Masonry.—Walls.—Constructional Carpentering.—Road Materials.—Road Construction.—Reinforced Concrete Construction.—Masonry Bridges and River Work.—Hydraulics.—Land Drainage.—Pumping Machinery and Stations.—The Use of Water Power.—Main Drainage.—Sewage Disposal.—Royal Commission on Sewage Disposal.—Salford Sewage Works.—Sanitation, House Drainage and Disinfection.—Refuse Disposal.—Waterworks, Preliminary Considerations and Sources of Supply.—Construction, Filtration and Purification.—Water-works.—Distribution.—Chimneys, Brick and Steel.—Steel Construction: Stanchions, Rivets and Bolts.—Steel Construction: Beams and Girders.—Combined Structures in Iron and Steel.—Specification.—Electric Tramways.—Appendix.—INDEX.

"A veritable *ode mecum* . . . would prove an acquisition to the library of any Municipal Engineer."—*Surveyor*.

In Medium Svo. Fully Illustrated. Cloth.

THE MAIN DRAINAGE OF TOWNS.

By F. NOEL TAYLOR, Civil Engineer.

CONTENTS.—Maps, Plans, Sections, and Preliminary Considerations.—Principles of Hydraulics and Hydrostatics.—Calculations in reference to Design of Sewage Works.—Practical Construction, Trenches, and Tunnels.—Forms of Sewers.—Ventilation of Sewers.—Manholes, Lamp-holes, Storm Overflows, etc.—Pumping Sewage.—House Drainage.—Sewage Disposal from a Theoretical Standpoint.—Sewage Disposal Works.—Special Constructions.—TABLES.—INDEX.

In Medium Svo. Handsome Cloth. With 116 Illustrations. 16s. net.

MODERN DESTROYER PRACTICE.

By W. FRANCIS GOODRICH, Assoc. Inst. C.E.,
F.I. San. Engrs., &c.

CONTENTS.—Some Alternative Methods of Refuse Disposal.—Representative Types of British Destroyers.—Systems of Charging Destroyers.—Destroyers combined with Sewage Works.—With Electricity Works.—Refuse Destruction in U.K.—Site.—Specifications.—Design and Operation.—Operative Costs.—Residuals.—Foreign and Colonial Practices.—INDEX.

In Crown Quarto. Handsome Cloth. Illustrated. 8s. 6d. net.

Building Construction in Earthquake Countries.

Translated from the Italian of ING. ALFREDO MONTELLI.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SEVENTEENTH EDITION. Thoroughly Revised Throughout, and Greatly Enlarged. Large 8vo. Cloth. Profusely Illustrated.

A MANUAL OF MARINE ENGINEERING:

COMPRISING THE DESIGNING, CONSTRUCTION, AND WORKING OF MARINE MACHINERY.

By A. E. SEATON, M.I.C.E., M.I.Mech.E., M.I.N.A.

GENERAL CONTENTS.—PART I.—Principles of Marine Propulsion. PART II.—Principles of Steam Engineering. PART III.—Details of Marine Engines: Design and Calculations for Cylinders, Pistons, Valves, Expansion Valves, &c. PART IV.—Propellers. PART V.—Boilers. PART VI.—Miscellaneous.

"The Student, Draughtsman, and Engineer will find this work the MOST VALUABLE HANDBOOK of Reference on the Marine Engine now in existence."—*Marine Engineer*

TENTH EDITION, Thoroughly Revised. Pocket-Size, Leather. 8s. 6d.

A POCKET-BOOK OF MARINE ENGINEERING RULES AND TABLES,

FOR THE USE OF

Marine Engineers, Naval Architects, Designers, Draughtsmen, Superintendents and Others.

By A. E. SEATON, M.I.C.E., M.I.Mech.E., M.I.N.A.

AND
H. M. ROUNTHWAITE, M.I.Mech.E., M.I.N.A.

"The best book of its kind, and the information is both up-to-date and reliable."—*Engineer*

In Large 8vo. Handsome Cloth. With Frontispiece, 6 Plates, 65 other Illustrations, and 60 Tables. 12s. 6d. net.

THE SCREW PROPELLER

And other Competing Instruments for Marine Propulsion.

By A. E. SEATON, M.INST.C.E., M.I.MECH.E., M.I.N.A.

"Contains all that is useful to know about the screw propeller. . . . Thoroughly up-to-date."—*Steamship*.

In Demj 8vo. Cloth. Fully Illustrated.

CALCULATIONS FOR MARINE ENGINEERS, AS REQUIRED AT BOARD OF TRADE EXAMS.,

Including Use of Logarithms.

By R. A. McMILLAN, B.Sc., WH. EX., EXTRA 1ST CLASS
ENGINEER (B.O.T.),

Head of the Engineering Department, Bootle Technical School.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET STRAND

SECOND EDITION, Revised and Enlarged. Pp. i-xv + 425.
With 377 Illustrations and 3 Folding Plates. 18s. net.

THE THEORY OF THE STEAM TURBINE.

A Treatise on the Principles of Construction of the Steam Turbine,
with Historical Notes on its Development.

By ALEXANDER JUDE.

CONTENTS.—Fundamental.—Historical Notes on Turbines.—The Velocity of Steam.—Types of Steam Turbines.—Practical Turbines.—The Efficiency of Turbines, Type I.—Trajectory of the Steam.—Efficiency of Turbines, Types II., III. and IV.—Turbine Vanes.—Disc and Vane Friction in Turbines.—Specific Heat of Superheated Steam.—Strength of Rotating Discs.—Governing Steam Turbines.—Steam Consumption of Turbines.—The Whirling of Shafts.—Speed of Turbines.—INDEX.

"One of the latest text-books . . . also one of the best . . . there is absolutely no padding."—*Sir William White* in the *Times* Engineering Supplement.

SEVENTH EDITION, Revised. Large Crown 8vo. Pp. i-xi + 394. With
5 Plates and 110 Illustrations in Text. 6s. net.

ENGINE-ROOM PRACTICE:

A Handbook for Engineers and Officers in the Royal Navy and Mercantile
Marine, including the Management of the Main and Auxiliary
Engines on Board Ship.

By JOHN G. LIVERSIDGE, ENGR.-COMM. R.N., A.M.I.C.E.

"This VERY USEFUL BOOK . . . ILLUSTRATIONS are of GREAT IMPORTANCE in a work of this kind, and it is satisfactory to find that SPECIAL ATTENTION has been given in this respect."—*Engineers' Gazette*.

In Large Crown 8vo. Cloth. Pp. i-xxviii + 244. With 25 Illustrations. 6s. net.

SEA WATER DISTILLATION.

By FRANK NORMANDY, of the Middle Temple, Barrister-at-Law.

CONTENTS.—Distilling Machinery.—Sea Water.—Steam.—Multiple Distillation.—The Evaporator.—The Distilling Condenser.—Pumping Machinery.—Useful Memoranda:—The Filter, Prevention of Corrosion and Decay of Metals, Removal of Scale, Cleaning, Overhauling, &c.—INDEX.

"The analytical treatment of the problem is concise and comprehensive in its scope."
—*Marine Engineer*.

FOURTH EDITION, Revised. Pocket-Size, Leather. Pp. i-xiii + 583.
12s. 6d.

BOILERS, MARINE AND LAND: THEIR CONSTRUCTION AND STRENGTH.

A HANDBOOK OF RULES, FORMULÆ, TABLES, &c., RELATIVE TO MATERIALS,
SCANTLINGS, AND PRESSURES, SAFETY VALVES, SPRINGS,
FITTINGS AND MOUNTINGS, &c.

FOR THE USE OF ENGINEERS, SURVEYORS, BOILER-MAKERS,
AND STEAM USERS.

By T. W. TRAILL, M. INST. O. E., F. E. R. N.,

Late Engineer Surveyor-in-Chief to the Board of Trade.

"Contains an ENORMOUS QUANTITY OF INFORMATION arranged in a very convenient form. . .
A MOST USEFUL VOLUME . . . supplying information to be had nowhere else."—*The Engineer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

THIRD EDITION, Revised. Pp. i-xv+356. With Frontispiece, 8 Plates and 218 Illustrations in the Text. 21s.

A MANUAL OF LOCOMOTIVE ENGINEERING:

A Practical Text-Book for the Use of Engine Builders,
Designers and Draughtsmen, Railway
Engineers, and Students.

By WILLIAM FRANK PETTIGREW, M.INST.C.E.

Contents.—Historical Introduction, 1763-1863.—Modern Locomotives: Simple.—Modern Locomotives: Compound.—Primary Consideration in Locomotive Design.—Cylinders, Steam Chests, and Stuffing Boxes.—Pistons, Piston Rods, Crossheads, and Slide Bars.—Connecting and Coupling Rods.—Wheels and Axles, Axle Boxes, Hornblocks, and Bearing Springs.—Balancing.—Valve Gear.—Slide Valves and Valve Gear Details.—Framing, Bogies and Axle Trucks, Radial Axle Boxes.—Boilers.—Smokebox, Blast Pipe, Firebox Fittings.—Boiler Mountings.—Tenders.—Railway Brakes.—Lubrication.—Consumption of Fuel, Evaporation and Engine Economy.—Repairs, Running, Inspection, and Renewals.—Three Appendices.—Index.

"The work contains all that can be learnt from a book upon such a subject. It will at once rank as the standard work upon this important subject."—*Railway Magazine.*

In Large 8vo. Pp. i-xxi+189. With Frontispiece and 148 other Illustrations. 8s. 6d. net.

LOCOMOTIVE COMPOUNDING AND SUPERHEATING.

By J. F. GAIRNS.

In Large 8vo. Handsome Cloth. Pp. i-xi+339. With 9 Plates. 16s.

LIGHT RAILWAYS AT HOME AND ABROAD.

By WILLIAM HENRY COLE, M.INST.C.E.,

Late Deputy-Manager, North-Western Railway, India.

"The whole subject is EXHAUSTIVELY and PRACTICALLY considered. The work can be cordially recommended as INDISPENSABLE to those whose duty it is to become acquainted with one of the prime necessities of the immediate future."—*Railway Official Gazette.*

THIRD EDITION, Revised and Enlarged. Large 8vo, Handsome Cloth. 25s. net.

Lubrication & Lubricants:

A Treatise on the Theory and Practice of Lubrication, and on the Nature, Properties, and Testing of Lubricants.

BY

LEONARD ARCHBUTT, F.I.C., F.C.S.,
Chemist to the Mid. Ry. Co.

AND

H. M. DEELEY, M.I.Mech.E., F.G.S.
Late Chief Loco. Super., Mid. Ry. Co.

CONTENTS.—I. Friction of Solids.—II. Liquid Friction or Viscosity, and Plastic Friction.—III. Superficial Tension.—IV. The Theory of Lubrication.—V. Lubricants, their Sources, Preparation, and Properties.—VI. Physical Properties and Methods of Examination of Lubricants.—VII. Chemical Properties and Methods of Examination of Lubricants.—VIII. The Systematic Testing of Lubricants by Physical and Chemical Methods.—IX. The Mechanical Testing of Lubricants.—X. The Design and Lubrication of Bearings.—XI. The Lubrication of Machinery.—INDEX.

"A most valuable and comprehensive treatise on a subject of the greatest importance to engineers."—*Engineering.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

In Crown 8vo, Handsome Cloth. Very Fully Illustrated.

MOTOR-CAR MECHANISM AND MANAGEMENT.

By W. POYNTER ADAMS, M.Inst.E.E.

PART I.—THE PETROL CAR. 5s. net.

THIRD EDITION. Revised and Greatly Enlarged.

"Should be carefully studied by those who have anything to do with motors."—*Automobile and Carriage Builders' Journal*.

PART II.—ELECTRICAL AND PETROL ELECTRICAL MOTOR CARS. 5s. net.

Pp. i-x + 202. With 50 Illustrations, including Frontispiece and 3 Plates, contains also 13 page Glossary.

"Cleverly written . . . will be found of considerable value."—*Practical Engineer*

In Large 8vo. Handsome Cloth. Pp. i,ix + 376. With 12 Folding Tables and 329 Illustrations. 18s. net

A MANUAL OF PETROL MOTORS AND MOTOR-CARS.

Comprising the Designing, Construction, and Working of Petrol Motors.

By F. STRICKLAND.

"Thoroughly practical and scientific. . . . We have pleasure in recommending it to all."—*Mechanical Engineer*.

In Medium 8vo. Handsome Cloth. Pp. i-xv + 272. With 306 Illustrations. 15s. net.

OIL MOTORS.

Their Development, Construction, and Management.

By G. LIECKFELD. (Authorised English Edition).

CONTENTS.—Liquid Fuels for Power Production.—Development of the Petrol and Paraffin Motors.—Working of the Later Paraffin and Petrol Engines.—Ignition Devices.—Examples of Stationary Petrol, Alcohol, Paraffin, and Crude Oil Engines.—Automobiles.—Ship, Boat, and Air-ship Engines.—Vehicles, &c., Driven by Internal Combustion Engines.—Erection and Attendance of Engines Driven with Liquid Fuel.—Correcting Irregularities in Running.

"One of the most comprehensive publications we have perused, and one that can be thoroughly recommended."—*Petroleum Review*.

In Medium 8vo. Handsome Cloth. Fully Illustrated.

THE GAS TURBINE, Theory, Construction, and Working Results of Two Machines in Actual Use.

By HANS HOLZWARTH.

Translated by A. P. CHALKLEY, B.Sc.

In Demy 8vo. Handsome Cloth. Pp. i-xi + 176. With 130 Illustrations. 6s. net.

CARBURETTORS, VAPORISERS, & VALVES, used in Internal Combustion Engines.

By EDWARD BUTLER, M.I.Mech.E.

"Mr. Butler writes with an intimate practical knowledge of his subject, and the book is one we have every pleasure in recommending."—*Mechanical Engineer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

FIFTH EDITION, Revised and Enlarged. With additional Illustrations.
Large 8vo, Handsome Cloth. 25s. net.

**A TEXT-BOOK ON
GAS, OIL, AND AIR ENGINES.**

By BRYAN DONKIN, M. INST. C. E., M. INST. MECH. E.

Revised throughout by T. GRAVES SMITH. With important New Matter
by Prof. BURSTALL.

"A very much up-to-date classic."—*Daily Telegraph*.

In Quarto, Handsome Cloth. With Numerous Plates. 25s.

**THE HEAT EFFICIENCY OF STEAM BOILERS
(LAND, MARINE, AND LOCOMOTIVE).**

With Tests and Experiments on Different Types, Heating Value of Fuels.
Analyses of Gases, Evaporation, and Suggestions for Testing Boilers.

By BRYAN DONKIN, M. INST. C. E.

"Probably the MOST EXHAUSTIVE resume that has ever been collected. A PRACTICAL
BOOK by a thoroughly practical man."—*Iron and Coal Trades Review*.

In Handsome Cloth. Fully Illustrated Throughout. 12s. 6d. net.

Internal Combustion Engines and Gas Producers.

By C. W. ASKLING, M. E., AND E. ROESLER, M. E.

CONTENTS.—Comparison of Internal Combustion and other Heat Engines.—The
Production, Preparation, Composition, and Qualities of Fuels used in Gas and Oil Engines.
—Gas Producers, with Accessories: General Principles of Design.—Management of
Suction-Gas Plant.—Producers for Power Purposes.—Principal Cycles of Internal Com-
bustion Engines.—Gas Engines.—Oil Engines.—Combustion.—INDEX.

In Large Crown 8vo. Cloth. Pp. i-vii + 198. With 55 Illustrations.
5s. net.

SUCTION GAS PLANTS.

By PROF. C. A. SMITH, of the East London Technical College.

"This book is one we can cordially recommend as affording a complete knowledge of
the theoretical aspect of Suction Plants."—*Gas World*.

In Handsome Cloth. Pp. i-iv + 262. With 93 Illustrations. 12s. 6d. net.

THE GAS TURBINE.

Progress in the Design and Construction of Turbines
Operated by Gases of Combustion.

By HENRY HARRISON SUPLEE, B. SC.

"Will be of considerable assistance to gas power engineers."—*Gas World*

In Large Crown 8vo. Handsome Cloth. 4s. 6d. net.

**THE THERMO-DYNAMIC PRINCIPLES OF
ENGINE DESIGN.**

By LIONEL M. HOBBS,

Engineer-Lieutenant, R.N.; Instructor in Applied Mechanics and Marine Engine
Design at the Royal Naval College, Greenwich

"Serves its purpose admirably . . . should prove of invaluable service . . . well
up-to-date."—*Shipping World*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Crown 8vo, Cloth. Illustrated with Diagrams. 3s. net.

THE FORCE OF THE WIND.

By HERBERT CHATLEY, B.Sc. ENG. (LOND.),

Professor of Civil Engineering, Tong Shan Engineering College, N. China.

CONTENTS.—Practical Importance of Wind Pressure.—Impulsive Force of the Wind.—Variations in Velocity.—Stream Line Theory.—Stress in Structures due to Wind.—Windmills.—Train and Motor Resistance.—Effect of Wind on Water.—Scouring Effect of Wind.—INDEX.

"Could not well be more terse or pointed."—*Symon's Meteorological Magazine*.

In Crown 8vo, Handsome Cloth. With 22 Diagrams. 3s. 6d. net.

STRESSES IN MASONRY.

By HERBERT CHATLEY, B.Sc. ENG. (LOND.).

CONTENTS.—Strength of Stone.—Walls.—Columns and Piers.—Brackets and Cantilevers.—Simple Arches.—Vaults and Skew Arches.—Domes.—Retaining Walls and Domes.—Artificial Stone.—Re-inforced Concrete.—INDEX.

"A most useful aid to surmounting the difficulties which this subject presents."—*Surveyor*.

In Handsome Cloth. With 11 Folding Tables. 12s. 6d. net.

EXPERIMENTAL INVESTIGATIONS ON THE POWER REQUIRED TO DRIVE ROLLING MILLS.

TRANSLATED FROM THE GERMAN OF J. PUPPÉ.

"The thoroughness with which the work is undertaken is exemplified in the Tables."—*Traffic*.

FIFTH EDITION. Pp. i-xii+157. With 50 Illustrations. Cloth, 4s. 6d.

STEAM - BOILERS;

THEIR DEFECTS, MANAGEMENT, AND CONSTRUCTION.

By R. D. MUNRO,

Chief Engineer of the Scottish Boiler Insurance and Engine Inspection Company.

"A valuable companion for workmen and engineers engaged about Steam Boilers, ought to be carefully studied, and ALWAYS AT HAND."—*Coll. Guardian*.

By THE SAME AUTHOR.

KITCHEN BOILER EXPLOSIONS: Why they Occur, and How to Prevent their Occurrence. A Practical Handbook based on Actual Experiment. With Diagram and Coloured Plate. 3s.

In Crown 8vo, Cloth. Pp. i-xii+180. With 143 Illustrations. 5s. net.

EMERY GRINDING MACHINERY.

A Text-Book of Workshop Practice in General Tool Grinding, and the Design, Construction, and Application of the Machines Employed.

By R. B. HODGSON, A.M. INST. MECH. E.

"Eminently practical . . . cannot fail to attract the notice of the users of this class of machinery, and to meet with careful perusal."—*Chem. Trade Journal*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Crown Quarto. Cloth. With 126 Figures, 88 Drawings, and sample Blue and White Prints, also Tracing. 10s. 6d. net.

AN ELEMENTARY TEXT-BOOK ON MECHANICAL DRAWING.

By JOHN E. JAGGER, M.Sc.(Vic.), WHIT. SCH.

"An admirable book . . . all the information it contains is of a thoroughly practical kind, and the numerous engravings accompanying the text cannot be praised too highly."—*Engineer*.

SIXTH EDITION, Thoroughly Revised and Greatly Enlarged. Pp. i-x+291. With 12 Plates and 262 other Illustrations. Price 9s. net.

VALVES AND VALVE-GEARING:

A Practical Text-book for the use of Engineers, Draughtsmen, and Students.

By CHARLES HURST, PRACTICAL DRAUGHTSMAN.

PART I.—Steam Engine Valves.	PART III.—Air Compressor Valves and Gearing.
PART II.—Gas Engine Valves and Gears.	PART IV.—Pump Valves.
PART V.—Safety and Relief Valves.	

"Mr. Hurst's VALVES and VALVE-GEARING will prove a very valuable aid, and tend to the production of Engines of SCIENTIFIC DESIGN and ECONOMICAL WORKING. . . . Will be largely sought after by Students and Designers."—*Marine Engineer*.

"As a practical treatise on the subject, the book stands without a rival."—*Mechanical World*.

Hints on Steam Engine Design and Construction. By CHARLES HURST, "Author of Valves and Valve Gearing." SECOND EDITION, Revised. In Paper Boards, 8vo., Cloth Back. Pp. i-vi+62. With 32 Illustrations. Price 1s. 6d. net.

CONTENTS.—I. Steam Pipes.—II. Valves.—III. Cylinders.—IV. Air Pumps and Condensers.—V. Motion Work.—VI. Crank Shafts and Pedestals.—VII. Valve Gear.—VIII. Lubrication.—IX. Miscellaneous Details.—INDEX.

"A handy volume which every practical young engineer should possess."—*The Model Engineer*.

FIFTH EDITION. In Two Parts, Published Separately.

A TEXT-BOOK OF Engineering Drawing and Design.

By SIDNEY H. WELLS, WH.Sc., A.M.I.C.E., A.M.I.MECH.E.

VOL. I.—PRACTICAL GEOMETRY, PLANE, AND SOLID.

Pp. i-xi+149. With 101 Illustrations, and an Appendix of 43 pages with 70 Illustrations. 4s. 6d.

VOL. II.—MACHINE AND ENGINE DRAWING AND DESIGN.

Pp. i-xi+321. With over 200 Illustrations. 4s. 6d.

"A CAPITAL TEXT-BOOK, ARRANGED ON AN EXCELLENT SYSTEM, calculated to give an intelligent grasp of the subject, and not the mere faculty of mechanical copying. . . . Mr. Wells shows how to make COMPLETE WORKING-DRAWINGS, discussing fully each step in the design."—*Electrician Review*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION, Enlarged. In Crown 8vo. Cloth. Pp. i-xiii + 463.
With 212 Illustrations. 6s. net.

PRACTICAL CALCULATIONS FOR ENGINEERS.

By CHARLES E. LARARD,

A.M.Inst.C.E., M.I.Mech.E., Wh.Eng.

Head of the Mechanical Engineering Department at the Northampton Institute, London, E.C.

AND H. A. GOLDING, A.M.I.Mech.E.

"Exactly what it should be in order to make it useful to students and practitioners of engineering."—*Manchester Guardian*.

SECOND EDITION. In Crown 8vo. Cloth. Pp. xiii + 302.
With 125 Illustrations. 5s. net.

MECHANICAL ENGINEERING FOR BEGINNERS.

By R. S. M'LAREN.

CONTENTS.—Materials.—Bolts and Nuts, Studs, Set Screws.—Boilers.—Steam Raising Accessories.—Steam Pipes and Valves.—The Steam Engine.—Power Transmission.—Condensing Plant.—The Steam Turbine.—Electricity.—Hydraulic Machinery.—Gas and Oil Engines.—Strength of Beams, and Useful Information.—INDEX.

"The best of its kind we have seen, and should be in the hands of every apprentice."
—*Steamship*.

SIXTH EDITION. Folio, strongly half-bound, 21s.

TRAVERSE TABLES:

Computed to Four Places of Decimals for every Minute of Angle
up to 100 of Distance.

For the Use of Surveyors and Engineers.

By RICHARD LLOYD GURDEN,

Authorised Surveyor for the Governments of New South Wales and Victoria.

* * * Published with the Concurrence of the Surveyors-General for New South
Wales and Victoria.

"Those who have experience in exact SURVEY-WORK will best know how to appreciate the enormous amount of labour represented by this valuable book. Every Surveyor in active practice has felt the want of such assistance few KNOWING OF THEIR (the Tables) PUBLICATION WILL REMAIN WITHOUT THEM."—*Engineer*.

Strongly Bound in Super Royal 8vo. Cloth Boards. 7s. 6d. net.

BONUS TABLES:

For Calculating Wages on the Bonus or Premium Systems.

For Engineering, Technical and Allied Trades.

By HENRY A. GOLDING, A.M.I.Mech.E.,

"Cannot fail to prove practically valuable to those for whom they have been designed."—*Scottman*.

HORSE-POWER COMPUTERS.

By H. A. GOLDING, A.M.I.Mech.E., A.M.I.A.E.

For Steam, Gas, and Oil Engines. Complete with Explanatory Pamphlet. In Box. 6s. net.

For Petrol Motors. Complete with Explanatory Pamphlet. In Envelope. 6d. net.

Detailed Prospectus on Application.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

• SECOND EDITION, Revised. In Crown 8vo, extra, with Diagrams and Folding-Plate. 7s. 6d. net.

THE CALCULUS FOR ENGINEERS AND PHYSICISTS,

INTEGRATION AND DIFFERENTIATION,
With Applications to Technical Problems;
AND
CLASSIFIED REFERENCE LIST OF INTEGRALS.

By PROF. ROBERT H. SMITH, A.M. INST. C.E., M.I. MECH. E., &c.

"Interesting diagrams, with practical illustrations of actual occurrence, are to be found herein in abundance. THE VERY COMPLETE CLASSIFIED REFERENCE TABLE will prove very useful in saving the time of those who want an integral in a hurry."—*The Engineer*.

In 4to, Boards. 7s. 6d.

MEASUREMENT CONVERSIONS

(English and French):

43 GRAPHIC TABLES OR DIAGRAMS, ON 28 PLATES.

Showing at a glance the MUTUAL CONVERSION OF MEASUREMENTS
IN DIFFERENT UNITS

Of Lengths, Areas, Volumes, Weights, Stresses, Densities, Quantities
of Work, Horse Powers, Temperatures, &c.

For the use of Engineers, Surveyors, Architects, and Contractors.

By PROF. ROBERT H. SMITH, A.M. INST. C.E., M.I. MECH. E., &c.

THIRD EDITION. Pocket Size, Leather Limp, with Gilt Edges and Rounded Corners,
printed on Special Thin Paper, with Illustrations, pp. 1-111 + 834. Price 18s. net.

THE MECHANICAL ENGINEER'S REFERENCE BOOK.

By HENRY HARRISON SUPLEE, B.Sc., M.E.

"We feel sure it will be of great service to mechanical engineers."—*Engineering*.

In Crown 8vo. Handsome Cloth. Profusely Illustrated. 2s. 6d. net.

ELEMENTARY GRAPHIC STATICS.

By W. J. CRAWFORD, D.Sc.,

Lecturer in Mechanical Engineering, The Municipal Technical Institute, Belfast.

ABRIDGED CONTENTS.—Introduction.—Some Easily Performed Experiments to
Illustrate the Simple Laws of Graphic Statics.—Miscellaneous Examples.—Parallel
Forces and Moments of Forces.—The Funicular or Link Polygon.—Solution of Frame-
works having External Loads.—The Force of Gravity.—The Use of Graphic Statics to
find Bending Moments and Shearing Forces.—Some Miscellaneous Practical Problems.—
APPENDIX.

With Diagrams. Crown 8vo. Cloth, 4s. 6d.

THE STUDENT'S MECHANICS:

An Introduction to the Study of Force and Motion.

By WALTER R. BROWNE, M.A., M. INST. C.E.

"Clear in style and practical in method, 'THE STUDENT'S MECHANICS' is cordially
recommended from all points of view."—*Athenaeum*.

By THE SAME AUTHOR.

FOUNDATIONS OF MECHANICS

Papers reprinted from the *Engineer*. In Crown 8vo, 1s.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY

ANDREW JAMIESON, M.INST.C.E., M.I.E.E., F.R.S.E.,
Formerly Professor of Electrical Engineering, The Glas. and W. of Scot. Tech. Coll.

PROFESSOR JAMIESON'S ADVANCED TEXT-BOOKS.

In Large Crown 8vo. Fully Illustrated.

STEAM AND STEAM-ENGINES, INCLUDING TURBINES AND BOILERS. For the Use of Engineers and for Students preparing for Examinations. With over 800 pp., over 400 Illustrations, 12 Plates, many B. of E., C. and G., Questions and Answers, and all Inst. C.E. Exams. on *Theory of Heat Engines*. Volume I. SEVENTENTH EDITION, Revised. 10s. 6d.

"The BEST BOOK yet published for the use of Students."—*Engineer*.

Volume II., dealing with Entropy; Air, Gas, Oil, and other Heat Engines. *At Press.*

APPLIED MECHANICS & MECHANICAL ENGINEERING.

In Five Volumes. Large Crown 8vo. *Including All the Inst. C.E. Exams.* in Section A, (1) Applied Mechanics; (2) Strength and Elasticity of Materials; (3a) Theory of Structures; Section B (Group ii.), Hydraulics; Theory of Machines. Also B. of E.; C. and G. Questions.

- VOL. I.—**Applied Mechanics.** EIGHTH EDITION. Pp. i-xviii + 400. 6s.
 ,, II.—**Strength of Materials.** EIGHTH EDITION. Pp. i-xviii + 314. 5s.
 ,, III.—**Theory of Structures.** EIGHTH EDITION. Pp. i-xviii + 232. 5s.
 ,, IV.—**Hydraulics.** EIGHTH EDITION. Pp. i-xvi + 274. 5s.
 ,, V.—**Theory of Machines.** SEVENTH EDITION. Pp. i-xx + 502. 7s. 6d.

*. * *In Five volumes, each complete in itself, and sold separately.*

PROFESSOR JAMIESON'S INTRODUCTORY MANUALS.

Crown 8vo. With Illustrations and Examination Papers.

HEAT ENGINES: STEAM, GAS AND OIL (Elementary Manual of). For First-Year Students, forming an Introduction to the Author's larger Work. THIRTEENTH EDITION, Revised and Enlarged. 7/6.

"Should be in the hands of EVERY engineering apprentice."—*Practical Engineer*.

MAGNETISM AND ELECTRICITY (Practical Elementary Manual of). For First-Year Students. With Stud. Inst. C.E. and B. of E. Exam. Questions. EIGHTH EDITION, Revised and Enlarged. 3/6.

"A THOROUGHLY TRUSTWORTHY Text-book. PRACTICAL and clear."—*Nature*.

APPLIED MECHANICS (Elementary Manual of). For First-Year Students. With B. of E., C. and G.; and Stud. Inst. C.E. Questions. NINTH EDITION, Revised and Greatly Enlarged. 3/6.

"The work has VERY HIGH QUALITIES, which may be condensed into the one word CLEAR."—*Science and Art*.

A POCKET-BOOK of ELECTRICAL RULES and TABLES.

For the Use of Electricians and Engineers. By JOHN MUNRO, C.E., and Prof. JAMIESON. Pocket Size. Leather, 8s. 6d. NINETEENTH EDITION. [See p. 31.]

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

WORKS BY W. J. MACQUORN RANKINE, LL.D., F.R.S.

Thoroughly Revised by W. J. MILLAR, C.E.

A MANUAL OF APPLIED MECHANICS: Comprising the Principles of Statics and Cinematics, and Theory of Structures, Mechanism, and Machines. With Numerous Diagrams. Crown 8vo, Cloth. EIGHTEENTH EDITION. 12s. 6d.

A MANUAL OF CIVIL ENGINEERING: Comprising Engineering Surveys, Earthwork, Foundations, Masonry, Carpentry, Metal Work, Roads, Railways, Canals, Rivers, Waterworks, Harbours, &c. With Numerous Tables and Illustrations. Crown 8vo, Cloth. TWENTY-FOURTH EDITION. 16s.

A MANUAL OF MACHINERY AND MILLWORK: Comprising the Geometry, Motions, Work, Strength, Construction, and Objects of Machines, &c. With nearly 300 Illustrations. Crown 8vo, Cloth. SEVENTH EDITION. 12s. 6d.

A MANUAL OF THE STEAM-ENGINE AND OTHER PRIME MOVERS. With a Section on GAS, OIL, and AIR ENGINES, by BRYAN DONKIN, M.Inst.C.E. With Folding Plates and Numerous Illustrations. Crown 8vo, Cloth. SEVENTEENTH EDITION. 12s. 6d.

USEFUL RULES AND TABLES: For Architects, Builders, Engineers, Founders, Mechanics, Shipbuilders, Surveyors, &c. With APPENDIX for the use of ELECTRICAL ENGINEERS. By Professor JAMIESON, M.Inst.C.E., M.I.E.E. EIGHTH EDITION. 10s. 6d.

A MECHANICAL TEXT-BOOK: A Practical and Simple Introduction to the Study of Mechanics. By Professor RANKINE and E. F. BAMBER, C.E. With Numerous Illustrations. Crown 8vo, Cloth. FIFTH EDITION. 9s.

*.† The "MECHANICAL TEXT-BOOK" was designed by Professor RANKINE as an INTRODUCTION to the above Series of Manuals.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

ELECTRICAL ENGINEERING.

SECOND EDITION, Revised. In Large 8vo. Cloth. Pp. i-xvi+496.
With 145 Illustrations, including 7 Plates. 24s. net.

CENTRAL ELECTRICAL STATIONS:

Their Design, Organisation, and Management.

By CHAS. H. WORDINGHAM, A.K.C., M.INST.C.E., M.INST.MECH.E.,
Late Memb. of Council Inst. E. E., and Electrical Engineer to the City of Manchester:
Electrical Engineer-in-Chief to the Admiralty.

"One of the MOST VALUABLE CONTRIBUTIONS to Central Station literature we have had for some time."—*Electricity.*

In Medium 8vo. Pp. i-xx+313. With 366 Figures and 23 Tables.
25s. net.

ELECTRIC CRANE CONSTRUCTION.

By CLAUDE W. HILL, A.M.INST.C.E. M.I.E.E., &c.

CONTENTS.—Overhead Cranes.—Locomotive and Portable Jib Cranes.—Derrick Cranes.—Transporters.—Sheer Legs.—Revolving Cantilever Cranes.—Cableways.—Power required for Crane Driving.—Starting Torque and Acceleration.—Design of Crane Structures.—Design of Machinery.—Brakes.—Toothed Gearing.—Hooks, Lifting Magnets, Ropes and Cranes.—Design of Magnets.—Motors, Controllers and Collectors.—Crane Installations.—INDEX.

"The whole work is straightforward, and may be recommended as being written from a thoroughly engineering point of view."—*Electrical Engineering.*

Large 8vo. Cloth. Pp. i-x+333 and 307 Illustrations. 16s. net.

ELECTRICITY METERS.

By HENRY G. SOLOMON, A.M.Inst.E.E.

"An earnest and successful attempt to deal comprehensively with modern methods of measuring current or power in electrical installations."—*Engineering.*

In Large 8vo. Handsome Cloth. Fully Illustrated. 21s. net.

TRANSFORMERS.

By HERMANN BOHLE, M.I.E.E.,

Prof. of Electrotechnics, S.A. College, Cape Town,

AND PROFESSOR DAVID ROBERTSON, B.Sc., A.I.E.E., OF BRISTOL.

CONTENTS.—General Principles.—Magnetising and No-Load Currents.—Losses in Transformers.—Iron Losses.—Copper Losses.—Temperature Rise.—Magnetic Leakage.—Leakage Inductance.—Vector Diagrams for Transformers.—Systematic Testing of Transformers.—Insulating Materials.—Examples of Construction.—Design of Transformers.—Applications of Transformers.—Regulating and Phase-Changing Transformers.—INDEX.

"This very complete treatise . . . model of what technical publications should be."—*Nature.*

In Large 8vo. Pp. i-x+116. With 79 Illustrations. 8s. 6d. net.

WIRELESS TELEGRAPHY.

By GUSTAVE EICHHORN, Ph.D.

"Well written . . . and combines with a good deal of description a careful investigation of the fundamental theoretical phenomena."—*Nature.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

A Large Crown Svo. Cloth. Pp. i-xvi+268. With 222 Illustrations.
5s. net.

TELEGRAPHIC SYSTEMS, AND OTHER NOTES.

A Handbook of the Principles on which Telegraphic Practice is Based.

By ARTHUR CROTCH, of the Engineer-in-Chief's Department, G. P. O.

CONTENTS.—Batteries, Primary and Secondary.—Universal Battery Working.—Duplex Telegraphy.—Duplex and Quadruplex Telegraphy.—Automatic Telegraphy.—Multiplex Telegraphy.—The Hughes Type Printing Instrument.—The Baudot System.—The Murray Type Printing Telegraph.—Test and Battery Boxes.—Circuit Concentration, &c.—Repeaters.—Submarine Telegraphy.—Wireless Telegraphy.—INDEX.—LIST OF DIAGRAMS OF CONNECTIONS.

"This book is a particularly good one . . . we can thoroughly recommend it . . . a handy book of ready reference."—*Electrical Review*.

"The treatise will be of much help to the telegraph engineer, and to the student in his preparatory training and it can be thoroughly recommended."—*Electrician*.

NINETEENTH EDITION. Leather, Pocket Size, with 810 pages. 8s. 6d.

A POCKET-BOOK OF ELECTRICAL RULES & TABLES

FOR THE USE OF ELECTRICIANS AND ENGINEERS.

By JOHN MUNRO, C.E., & PROF. JAMIESON, M. INST. C.E., F.R.S.E.

"Wonderfully Perfect. . . . Worthy of the highest commendation we can give it."—*Electrician*.

GRIFFIN'S ELECTRICAL PRICE-BOOK: For Electrical, Civil, Marine, and Borough Engineers, Local Authorities, Architects, Railway Contractors, &c. Edited by H. J. DOWSING. SECOND EDITION. 8s. 6d.

In Large Crown Svo. Handsome Cloth. 15s. net.

ELECTRICAL THEORY AND THE PROBLEM OF THE UNIVERSE.

By G. W. DE TUNZELMANN, B.Sc., LONDON,

Member of the Institute of Electrical Engineers; formerly Professor of Natural Philosophy and Astronomy, H.M.S. "Britannia," Dartmouth.

CONTENTS.—Fundamental Electrical Phenomena.—Units and Measurement.—Meaning and Possibility of a Mechanical Theory of Electricity.—The Ether.—The Ether as a Framework of Reference for Motion.—The Relations between Ether and Moving Matter.—Electric Conduction in Gases.—The Faraday-Maxwell Theory.—The Electron Theory.—Magnetism and the Dissipation of Energy.—Contract Electrification and Electrolysis.—Metallic Conduction.—Optical Phenomena.—The Mechanism of Radiation.—General Phenomena of Radio Activity.—Transmutations of Radio-Active Substances.—Ages of the Sun and Earth.—The Solar Corona, The Aurora, and Comets' Tails.—Radio-Activity in Stars and Nebulae.—Arrangement and Number of Atoms in a Molecule.—Changes in the Aspect of Fundamental Mechanical Principles.—Gravitation and Cohesion.—The Place of Mind in the Universe.—Mathematical and other Appendices.—INDEX.

"One of the most valuable contributions to electrical literature the year has produced."—*Times*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Large Svo. Handsome Cloth. Fully Illustrated.

ELECTRICAL PHOTOMETRY.

By PROF. HERMANN BOHLE, M.I.E.E.,

Professor of Electrotechnics, S. A. College, Cape Town.

THIRD EDITION. *In Handsome Cloth. Revised, Enlarged, and Re-written. Pp. i-xv + 425. Fully Illustrated. 12s. 6d. net.*

A TREATISE ON

ELECTRO-METALLURGY:

Embracing the Application of Electrolysis to the Plating, Depositing, Smelting, and Refining of various Metals, and to the Reproduction of Printing Surfaces and Art-Work, &c.

By W. G. McMILLAN, F.I.C., AND W. R. COOPER, M.A., B.Sc.
(See also page 53.)

SECOND EDITION. *Thoroughly Revised and Enlarged. In Large Svo. With Numerous Illustrations and Three Folding Plates. 21s. net.*

ELECTRIC SMELTING & REFINING:

A Practical Manual of the Extraction and Treatment of Metals by Electrical Methods.

Being the "ELEKTRO-METALLURGIE" of DR. W. BORCHERS.

Translated from the Latest German Edition

By WALTER G. McMILLAN, F.I.C., F.C.S.

(See also page 53.)

THIRD EDITION. *In Crown Svo. Handsome Cloth. With 30 New Illustrations. 7s. 6d. net.*

Electrical Practice in Collieries.

By PROF. D. BURNS, M.E., M.Inst.M.E.,

Professor of Mining and Geology to the Glasgow and West of Scotland Technical College.

Units of Measurement, Conductors, &c.—The Theory of the Dynamo.—The Dynamo: Details of Construction and Working.—Motors.—Lighting Installations in Collieries.—Pumping by Electricity.—Electrical Haulage.—Coal Cutting.—Miscellaneous Applications of Electricity in Mines.—Coal Mines Regulation Act (Electricity).—INDEX.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

*In Large Svo. Handsome Cloth. Profusely Illustrated. In Two VOLUMES, Each Complete in itself, and SOLD SEPARATELY.

THE DESIGN AND CONSTRUCTION OF SHIPS.

By JOHN HARVARD BILES, M.Inst.N.A.,
Professor of Naval Architecture in Glasgow University.

Volume I.—CALCULATIONS AND STRENGTH. With 36 Folding Plates, and 245 other Illustrations. Pp. i-viii+423. Complete with Index. 25s. net.

CONTENTS.—PART I.—Areas, Volumes, and Centres of Gravity. PART II.—Ship Calculations. PART III.—Strength of Ships.

"No teacher of naval architecture nor scientifically-equipped student of the same subject can afford to be without it . . . A work with up-to-date information which will doubtless remain the standard for many years."—*Times' Engineering Supplement.*

Volume II.—STABILITY, RESISTANCE, PROPULSION, AND OSCILLATIONS OF SHIPS. With 4 Folding Plates and 316 other Illustrations. Pp. i-x+430. Complete with Index. 25s. net.

CONTENTS.—PART IV.—Stability. PART V.—Resistance. PART VI.—Propulsion. PART VII.—Oscillations of Ships.

"This able treatise is one which no one engaged in ship-designing can afford to be without."—*Shipbuilder.*

Royal Run Handsome Cloth. With numerous Illustrations and Tables. 25s.

THE STABILITY OF SHIPS.

By SIR EDWARD J. REED, K.C.B., F.R.S., M.P.,

"SIR EDWARD REED'S 'STABILITY OF SHIPS' IS INVALUABLE. THE NAVAL ARCHITECT will find brought together and ready to his hand, a mass of information which he would otherwise have to seek in an almost endless variety of publications, and some of which he would possibly not be able to obtain at all elsewhere."—*Steamship.*

AERONAUTICAL ENGINEERING.

SECOND EDITION, Revised. In Large Svo. Cloth. With many Illustrations. 10s. 6d. net.

THE PROBLEM OF FLIGHT.

A TEXT-BOOK OF AERIAL ENGINEERING.

By HERBERT CHATLEY, B.Sc.(ENG.), LONDON,
Professor of Civil Engineering, Tong Shan Engineering College, N. China.

CONTENTS.—The Problem of Flight.—The Helix.—The Aeroplane.—The Airplane.—Dirigible Balloons.—Form and Fittings of the Airship.—APPENDICES (*The Possibility of Flight, Weight, A Flexible Wing, Theory of Balance, Bibliography*).—INDEX.
"An epitome of the knowledge available on the subject."— *Scotsman.*

In Handsome Cloth. Illustrated. Pocket Size. 2s. 6d. net.

A COMPENDIUM OF AVIATION AND AEROSTATION, Balloons, Dirigibles and Flying Machines.

By LIEUT.-COL. H. HOERNES.

Translated and Supplemented with Facts of Interest to English readers—i.e., details regarding British Dirigibles, Aeroplanes, Flying Grounds, &c.—with an Introduction and Biographical Sketch of the Author by J. H. LEIBSOER, Editor of *Aeronautics.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY THOMAS WALTON,
NAVAL ARCHITECT.

FOURTH EDITION. Pp. i-xvi + 332. With 18 Plates and 237 other
Illustrations, including 59 Folding Diagrams. 18s. net.

STEEL SHIPS:
THEIR CONSTRUCTION AND MAINTENANCE.

*A Manual for Shipbuilders, Ship Superintendents, Students,
and Marine Engineers.*

By THOMAS WALTON, NAVAL ARCHITECT,
AUTHOR OF "KNOW YOUR OWN SHIP."

CONTENTS.—I. Manufacture of Cast Iron, Wrought Iron, and Steel.—Com-
position of Iron and Steel, Quality, Strength, Tests, &c. II. Classification of
Steel Ships. III. Considerations in making choice of Type of Vessel.—Framing
of Ships. IV. Strains experienced by Ships.—Methods of Computing and
Comparing Strengths of Ships. V. Construction of Ships.—Alternative Modes
of Construction.—Types of Vessels.—Turret, Self Trimming, and Trunk
Steamers, &c.—Rivets and Rivetting, Workmanship. VI. Pumping Arrange-
ments. VII. Maintenance.—Prevention of Deterioration in the Hulls of
Ships.—Cement, Paint, &c.—INDEX.

"So thorough and well written is every chapter in the book that it is difficult to select
any of them as being worthy of exceptional praise. Altogether, the work is excellent, and
will prove of great value to those for whom it is intended."—*The Engineer*.

In Cloth. Pp. i-xii. + 224. With 9 Plates and 163 other Illustrations,
including 40 Folding Diagrams. 7s. 6d. net.

PRESENT-DAY SHIPBUILDING.

For Shipyard Students, Ships' Officers, and Engineers.

By THOS. WALTON.

GENERAL CONTENTS.—Classification.—Materials used in Shipbuilding.—
Alternative Modes of Construction.—Details of Construction.—Framing,
Plating, Rivetting, Stem Frames, Twin-Screw Arrangements, Water
Ballast Arrangements, Loading and Discharging Gear, &c.—Types of
Vessels, including Atlantic Liners, Cargo Steamers, Oil carrying Steamers,
Turret and other Self Trimming Steamers, &c.—INDEX.

"Simple language . . . clear and easily followed illustrations."—*Times
Engineering Supplement*.

"We heartily recommend it to all who have to do with ships."—*Steamship*.

TWELFTH EDITION. In Crown 8vo. Cloth. Pp. i-xvi + 363. With
142 Illustrations, including 2 Folding Diagrams. 7s 6d.

The Chapters on Tonnage and Freeboard have been brought thoroughly
up to date, and embody the latest (1906) Board of Trade Regulations on
these subjects.

KNOW YOUR OWN SHIP.

By THOMAS WALTON, NAVAL ARCHITECT.

*Specially arranged to suit the requirements of Ships' Officers, Shipowners
Superintendents, Draughtsmen, Engineers, and Others.*

CONTENTS.—Displacement and Deadweight.—Moments.—Buoyancy.—Strain.—
Structure.—Stability.—Rolling.—Ballasting.—Loading.—Shifting Cargoes.—Effect
of Admission of Water into Ship.—Trim Tonnage.—Freeboard (Load-line).—Calculations.—
Set of Calculations from Actual Drawings.—INDEX.

"The work is of the highest value, and all who go down to the sea in ships should make them-
selves acquainted with it."—*Shipping World* (on the new edition).

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

• **GRIFFIN'S NAUTICAL SERIES.**

FIFTH EDITION, *Thoroughly Revised.* Pp. i-xvi + 243. With Frontispiece, 24 Plates (3 Coloured), and 63 Illustrations in the Text and new Chapter on Clouds. Price 6s.

**A MANUAL OF
ELEMENTARY SEAMANSHIP.**

BY

D. WILSON-BARKER, MASTER MARINER; F.R.S.E., F.R.G.S., &c., &c.
YOUNGER BROTHERS OF THE TRINITY HOUSE.

GENERAL CONTENTS.—The Building of a Ship, Parts of Hull, Masts, &c.—Ropes, Knots, Splicing, &c.—Gear, Lead and Log, &c.—Rigging, Anchors—Sailmaking—The sails, &c.—Handling of Boats under Sail—Signals and Signalling—Rule of the Road—Keeping and Relieving Watch—Points of Etiquette—Glossary of Sea Terms and Phrases—Index.

"THIS ADMIRABLE MANUAL by CAPT. WILSON-BARKER of the 'Worcester,' seems to be PERFECTLY DESIGNED, and holds its place excellently in 'GRIFFIN'S NAUTICAL SERIES.' Although intended for those who are to become Officers of the Merchant Navy, it will be found useful by ALL YACHTSMEN."—*Athenaeum*

SECOND EDITION, *Revised.* Pp. i-xii + 156. With 61 Illustrations. Price 3s. 6d.

**NAVIGATION:
PRACTICAL AND THEORETICAL.**

By DAVID WILSON-BARKER, R.N.R., F.R.S.E., &c., &c.,

AND

WILLIAM ALLINGHAM,

FIRST-CLASS HONOURS, NAVIGATION, SCIENCE AND ART DEPARTMENT.

With Numerous Illustrations and Examination Questions.

GENERAL CONTENTS.—Definitions—Latitude and Longitude—Instruments of Navigation—Correction of Courses—Plane Sailing—Traverse Sailing—Day's Work—Parallel Sailing—Middle Latitude Sailing—Mercator's Chart—Mercator Sailing—Current Sailing—Position by Bearings—Great Circle Sailing—The Tides—Questions—Appendix: Compass Error—Numerous Useful Hints &c.—Index.

"A CAPITAL LITTLE BOOK . . . specially adapted to the New Examinations. The Authors are CAPT. WILSON-BARKER (Captain-Superintendent of the Nautical College, H.M.S. 'Worcester,' who has had great experience in the highest problems of Navigation), and MR. ALLINGHAM, a well-known writer on the Science of Navigation and Nautical Astronomy."—*Shipping World*.

Handsome Cloth. Pp. i-xvi + 132. With 10 Plates and 34 other Illustrations. Price 7s. 6d.

**MARINE METEOROLOGY,
FOR OFFICERS OF THE MERCHANT NAVY.**

By WILLIAM ALLINGHAM,

Joint Author of "Navigation, Theoretical and Practical."

With numerous Plates, Maps, Diagrams, and Illustrations, and a facsimile Reproduction of a Page from an actual Meteorological Log-Book.

"Quite the BEST publication, AND certainly the MOST INTERESTING, on this subject ever presented to Nautical men."—*Shipping Gazette*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

GRIFFIN'S NAUTICAL SERIES.

THIRD EDITION, REVISED. Pp. i-xii+175. With 54 Illustrations.
Price 3s. 6d.

PRACTICAL MECHANICS:
Applied to the Requirements of the Sailor.

By THOS. MACKENZIE, *Master Mariner, F.R.A.S.*

GENERAL CONTENTS.—Resolution and Composition of Forces—Work done by Machines and Living Agents—The Mechanical Powers: The Lever; Derricks as Bent Levers—The Wheel and Axle; Windlass; Ship's Capstan; Crab Winch—Tackles: the "Old Man"—The Inclined Plane; the Screw—The Centre of Gravity of a Ship and Cargo—Relative Strength of Rope: Steel Wire, Manilla, Hemp, Coir—Derricks and Shears—Calculation of the Cross-breaking Strain of Fir Spar—Centre of Effort of Sails—Hydrostatics: the Diving-bell; Stability of Floating Bodies; the Ship's Pump, &c.

"WELL WORTH the money . . . will be found EXCEEDINGLY HELPFUL."
Shipping World.

"NO SHIPS' OFFICERS' BOOKCASE will henceforth be complete without CAPTAIN MACKENZIE'S 'PRACTICAL MECHANICS.' Notwithstanding my many years' experience at sea, it has told me *how much more there is to acquire.*"—
(Letter to the Publishers from a Master Mariner).

WORKS BY RICHARD C. BUCK,

of the Thames Nautical Training College, H.M.S. 'Worcester.'

FOURTH EDITION, Revised and Corrected. Pp. i-viii+113.
With 38 Illustrations. Price 3s. 6d.

A MANUAL OF TRIGONOMETRY:

With Diagrams, Examples, and Exercises.

"* Mr. Buck's Text-Book has been SPECIALLY PREPARED with a view to the Examinations of the Board of Trade, in which Trigonometry is an obligatory subject.

"This ESSENTIALLY PRACTICAL and RELIABLE VOLUME."—*Schoolmaster*

SECOND EDITION, Revised. Pp. i-viii+158. Price 3s. 6d.

A MANUAL OF ALGEBRA.

Designed to meet the Requirements of Sailors and others.

"* These elementary works on ALGEBRA and TRIGONOMETRY are written specially for those who will have little opportunity of consulting a Teacher. They are books for "SELF-HELP." All but the simplest explanations have, therefore, been avoided, and answers to the Exercises are given. Any person may readily, by careful study, become master of their contents, and thus lay the foundation for a further mathematical course, if desired. It is hoped that to the younger Officers of our Mercantile Marine they will be found decidedly serviceable. The Examples and Exercises are taken from the Examination Papers set for the Cadets of the "Worcester."

"Clearly arranged, and well got up. . . . A first-rate Elementary Algebra."
Nautical Magazine.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

GRIFFIN'S NAUTICAL SERIES.

SECOND EDITION, Revised. With Diagrams. Price 2s.

LATITUDE AND LONGITUDE; How to Find them.

By W. J. MILLAR, C.E.,

Late Secretary to the Inst. of Engineers and Shipbuilders in Scotland."CONCISELY and CLEARLY WRITTEN . . . cannot but prove an acquisition to those studying Navigation."—*Marine Engineer.*"Young Seamen will find it HANDY and USEFUL, SIMPLE and CLEAR."—*The Engineer.*

THIRD EDITION, Revised. In Crown 8vo. Pp. i-xv+268. Price 5s.

THE LEGAL DUTIES OF SHIPMASTERS.

By BENEDICT WM. GINSBURG, M.A., LL.D. (OANTAB.),

Of the Inner Temple and Northern Circuit; Barrister-at-Law.

General Contents.—Qualification for Position of Shipmaster.—Contract with Shipowner.—Duty in respect of the Crew: Engagement; Apprentices; Discipline; Provisions, Accommodation, and Medical Comforts; Payment of Wages and Discharge.—Passengers.—Financial Responsibilities.—Cargo.—Casualty.—Duty to certain Public Authorities.—Pilots, Signals, Flags, and Light Dues.—Arrival at the Port of Discharge.—Appendices on Legal Matters: B.O.T. Certificates, Dietary Scales, Stowage of Grain Cargoes, Load Line Regulations, Life-saving Appliances, Carriage of Cattle.—INDEX.

"No intelligent Master should fail to add this to his list of necessary books. A few lines of it may save a LAWYER'S FEE, BESIDES ENDLESS WORRY."—*Liverpool Journal of Commerce.*

FIRST AID AT SEA.

THIRD EDITION, Revised. Pp. i-xviii+349. With 82 Illustrations and the latest Regulations on the Carriage of Medical Stores. 6s.

A MEDICAL AND SURGICAL HELP

For Shipmasters and Officers in the Merchant Navy.

By WM. JOHNSON SMITH, F.R.C.S.,

Principal Medical Officer, Seamen's Hospital, Greenwich.

*The attention of all interested in our Merchant Navy is requested to this exceedingly useful and valuable work. It is needless to say that it is the outcome of many years' PRACTICAL EXPERIENCE amongst Seamen.

"SOUND, JUDICIOUS, REALLY HELPFUL."—*The Lancet.*

TWELFTH EDITION, Revised and Enlarged. Price 7s. 6d.

KNOW YOUR OWN SHIP.

By THOMAS WALTON, NAVAL ARCHITECT.

Specially arranged to suit the requirements of Ships' Officers, Shipowners, Superintendents, Draughtsmen, Engineers, and Others.

For Contents and further particulars of this work, and other works by the same author, see p. 34.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

OTHER WORKS OF INTEREST TO SAILORS.

In Crown 8vo. Cloth. Fully Illustrated. 2s. 6d. net.

NOTES ON THE PRACTICAL DUTIES OF SHIPMASTERS.

By CAPT. W. HARRY WILKES, LIEUT. R.N.R., &c.

"We should like to commend this volume to the attention of all Officers in Command . . . a compact and concise mass of information."—*Shipping World*.

In Pocket Size. With 368 Pages. 3s. 6d. net.

ENGLISH-SPANISH AND SPANISH-ENGLISH SEA TERMS AND PHRASES.

By FLEET-PAYMASTER GRAHAM-HEWLETT.

"Most complete . . . useful . . . we can heartily recommend it."—*Steamship*.

In Crown 8vo. Handsome Cloth. Many Diagrams. 2s. 6d. net.

DEFINITIONS IN NAVIGATION & NAUTICAL ASTRONOMY.

By P GROVES-SHOWELL,

Head of the Navigation Department, L.C.C. School, Poplar.

CONTENTS.—Definitions.—General.—Navigation.—Nautical Astronomy.—Time.—Miscellaneous.—Notes. Measurements.—Mariner's Compass.—Chronometer.—Azimuth Compass.—Pelorus.—Sextant.—Vernier.—Artificial Horizon.—Sounding Machine.—Log.—Station Pointer.—Barometer.—Thermometer.—Hygrometer.—Hydrometer. Miscellaneous.—Star Nomenclature.—Greek Alphabet.—Planetary Symbols.—Weights and Measures.—Areas.—Volumes.—Useful Notes.—INDEX.

"Mr. Groves-Showell writes with a full knowledge of his subject, and with admirable clearness."—*Shipbuilder*.

Attention is also drawn to the following:—

HYDROGRAPHIC SURVEYING. By COMMANDER S. MESSUM, R.N. [See page 16.]

THEODOLITE SURVEYING. By Professor JAMES PARK. [See page 41.]

THE FORCE OF THE WIND. By HERBERT CHATLEY, B.Sc. [See page 24.]

THE EARTH'S ATMOSPHERE. By Dr. T. L. PHIPSON. [See page 46.]

WIRELESS TELEGRAPHY. By GUSTAVE EICHORN, Ph.D. [See page 30.]

LONDON: CHARLES GRIFFIN & CO., LIMITED, 11, BATTERY STREET, STRAND.

WORKS BY
SIR CLEMENT LE NEVE FOSTER, D.Sc., F.R.S.

SIXTH EDITION. With Frontispiece and 712 Illustrations. Price 28s. net.

ORE & STONE MINING.

BY SIR C. LE NEVE FOSTER, D.Sc., F.R.S.,
LATE PROFESSOR OF MINING, ROYAL COLLEGE OF SCIENCE.

REVISED, AND BROUGHT UP-TO-DATE

BY PROF. S. H. COX, ASSOC.R.S.M.,
PROFESSOR OF MINING, ROYAL COLLEGE OF SCIENCE.

GENERAL CONTENTS.

INTRODUCTION. Mode of Occurrence of Minerals.—Prospecting.—Boring.—Breaking Ground.—Supporting Excavations.—Exploitation.—Haulage or Transport.—Hoisting or Winding.—Drainage.—Ventilation.—Lighting.—Descent and Ascent.—Dressing.—Principles of Employment of Mining Labour.—Legislation affecting Mines and Quarries.—Condition of the Miner.—Accidents.—Index

"We have seldom had the pleasure to review a work so thorough and complete as the present one. Both in manner and in matter it is FAR SUPERIOR TO ANYTHING ON ITS SPECIAL SUBJECT HITHERTO PUBLISHED IN ENGLAND."—*Athenæum*.

"Not only is this work the acknowledged text-book on metal mining in Great Britain and the Colonies, but that it is so regarded in the United States of America is evidenced by the fact that it is the book on that subject recommended to the students in most of the mining schools of that country."—*The Times*.

SECOND EDITION, Revised. In Crown 8vo. Handsome Cloth.
With nearly 300 Illustrations. Price 7s. 6d. net.

THE ELEMENTS OF MINING AND QUARRYING.

An Introductory Text-Book for Mining Students.

BY SIR C. LE NEVE FOSTER, D.Sc., F.R.S.,
Late Professor of Mining at the Royal College of Science.

Revised by Prof. S. H. Cox, A.R.S.M., &c.

GENERAL CONTENTS.—INTRODUCTION.—Occurrence of Minerals.—Prospecting.—Boring.—Breaking Ground.—Supporting Excavations.—Exploitation.—Haulage or Transport.—Hoisting or Winding.—Drainage.—Ventilation.—Lighting.—Descent and Ascent.—Dressing, &c.—INDEX.

"A remarkably clear survey of the whole field of mining operations."—*Engineer*.

"Rarely does it fall to the lot of a reviewer to have to accord such unqualified praise as this book deserves. . . . The profession generally have every reason to be grateful to Sir C. Le Neve Foster for having enriched educational literature with so admirable an elementary text-book."—*Mining Journal*.

In Crown 8vo. Handsome Cloth. Illustrated. 5s. net.

METHODS OF AIR ANALYSIS.

BY J. S. HALDANE, M.D., LL.D., F.R.S.,
Reader in Physiology and Fellow of New College, Oxford.

An Account of Methods of Air Analysis suitable for work in Physiology, Hygiene, Investigations of Mine Air, Flue Gases, Exhaust Gases from Engines, &c.

In Crown 8vo. Handsome Cloth. Illustrated.

THE AIR OF MINES.

BY JOHN CADMAN, D.Sc., Prof. of Mining, University of Birmingham,
AND J. S. HALDANE, M.D., LL.D., F.R.S.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

WORKS ON COAL-MINING.

FIFTH EDITION, Revised and Greatly Enlarged. With 4 Plates and 690 Illustrations. Price 24s. net.

A TEXT-BOOK OF COAL-MINING:

FOR THE USE OF COLLIERY MANAGERS AND OTHERS
ENGAGED IN COAL-MINING.

By HERBERT WILLIAM HUGHES, F.G.S.,
Assoc. Royal School of Mines, General Manager of Sandwell Park Colliery.

GENERAL CONTENTS.—Geology.—Search for Coal.—Breaking Ground.—Sinking.—Preliminary Operations.—Methods of Working.—Haulage.—Winding.—Pumping.—Ventilation.—Lighting.—Works at Surface.—Preparation of Coal for Market.—INDEX.

"Quite the BEST BOOK of its kind . . . as PRACTICAL in aim as a book can be . . . The illustrations are EXCELLENT."—*Athenæum*.

"We cordially recommend the work."—*Colliery Guardian*.

"Will soon come to be regarded as the STANDARD WORK of its kind."—*Birmingham Daily Gazette*.

FIFTH EDITION, Thoroughly Revised and Greatly Enlarged. Re-set throughout. Large Crown 8vo. Handsome Cloth.

PRACTICAL COAL-MINING;

A MANUAL FOR MANAGERS, UNDER-MANAGERS,
COLLIERY ENGINEERS, AND OTHERS.

With Worked-out Problems on Haulage, Pumping, Ventilation, &c.

By GEORGE L. KERR, M.E., M.INST.M.E.

CONTENTS.—The Sources and Nature of Coal.—The Search for Coal.—Sinking.—Explosives.—Mechanical Wedges.—Rock Drills and Coal-cutting Machines.—Coal-cutting by Machinery.—Transmission of Power.—Modes of Working.—Timbers.—Roadways.—Winding Coal.—Haulage.—Pumping.—Ventilation.—Safety Lamps.—Surface Arrangements, Surveying, Levelling, &c.

"AN ESSENTIALLY PRACTICAL WORK, and can be confidently recommended. No department of Coal-Mining has been overlooked."—*Engineers' Gazette*.

THIRD EDITION, Revised. In Crown 8vo. Handsome Cloth.

ELEMENTARY COAL-MINING:

FOR THE USE OF STUDENTS, MINERS, AND OTHERS
PREPARING FOR EXAMINATIONS.

By GEORGE L. KERR, M.E., M.INST.M.E.

CONTENTS.—Sources and Nature of Coal.—Exploration and Boring for Coal.—Breaking Ground.—Explosives, Blasting, &c.—Sinking and Fitting of Shafts.—Modes of Working.—Timbering Roadways.—Winding and Drawing.—Haulage.—Pumping and Drainage.—Ventilation.—Cleaning and Sorting Coal.—Surveying, &c.

"An abundance of information conveyed in a popular and attractive form. . . . Will be of great use to all who are in any way interested in coal mining."—*Scottish Critic*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STP^{AND}

- FOURTEENTH EDITION, Revised. With Numerous Diagrams.
Cloth, 7s. 6d.

A TREATISE ON MINE-SURVEYING:

*For the use of Managers of Mines and Collieries, Students
at the Royal School of Mines, &c.*

By BENNETT H. BROUGH, ASSOC.R.S.M., F.G.S.

Revised by S. WARREN PRICE, Professor of Mine Surveying in
University College of South Wales and Monmouthshire.

CONTENTS. — General Explanations. — Measurement of Distances. — Miners Dial. — Variation of the Magnetic Needle. — Surveying with the Magnetic Needle in the Presence of Iron. — Surveying with the Fixed Needle. — The German Dial. — The Theodolite. — Traversing Underground. — Surface Surveys with the Theodolite. — Plotting the Survey. — Calculation of Areas. — Levelling. — Connection of the Underground and Surface Surveys. — Measuring Distances by Telescope. — Setting-out. — Mine-Surveying Problems. — Mine Plans. — Application of the Magnetic Needle in Mining. — Photographic Surveys. — APPENDICES. — INDEX.

"ITS CLARNESS OF STYLE, LUCIDITY OF DESCRIPTION, and FULLNESS OF DETAIL, have long ago won for it a place unique in the literature of this branch of mining engineering, and the present edition fully maintains the high standard of its predecessors. To the student, and to the mining engineer alike, ITS VALUE is inestimable. The illustrations are excellent."—*The Mining Journal*.

In Crown 8vo. Handsome Cloth. Fully Illustrated. 7s. 6d. net.

A HANDBOOK ON

THEODOLITE SURVEYING AND LEVELLING.

For the use of Students in Land and Mine Surveying.

By PROFESSOR JAMES PARK, F.G.S.

CONTENTS. — The Scope and Object of Surveying. — Land Surveying. — The Theodolite. — Chains and Steel Bands. — Obstacles to Allignment. — Meridian and Bearings. — The Theodolite Traverse. — Co-ordinates of a Station. — Calculation of Omitted or Connecting Line in a Traverse. — Calculation of Areas. — Subdivision of Land. — Triangulation. — Determination of True Meridian, Latitude and Time. — Levelling. — Railway Curves. — Mine Surveying. — Surveying Boreholes. — INDEX.

"A book which should prove as useful to the professional surveyor as to the student."—*Nature*.

SECOND EDITION, Revised. Crown 8vo. Handsome Cloth. Illustrated.
6s. net.

MINING GEOLOGY.

A TEXT-BOOK FOR MINING STUDENTS AND MINERS.

By PROF. JAMES PARK, F.G.S., M.Inst.M.M.,

Professor of Mining and Director of the Otago University School of Mines; late Director
Thames School of Mines, and Geological Surveyor and Mining Geologist to the
Government of New Zealand

GENERAL CONTENTS. — Introduction. — Classification of Mineral Deposits. — Ore Veins, their Filling, Age, and Structure. — The Dynamics of Lodes and Beds. — Ore Deposits Genetically Considered. — Ores and Minerals Considered Economically. — Mine Sampling and Ore Valuation. — The Examination and Valuation of Mines. — INDEX.

"A work which should find a place in the library of every mining engineer."—*Mining World*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS FOR MINERS AND STUDENTS.

THIRD EDITION. In Crown 8vo. Handsome Cloth. With 30 New Illustrations. 7s. 6d. net.

ELECTRICAL PRACTICE IN COLLIERIES.

By PROF. D. BURNS, M.E., M. INST. M.E.,

Professor of Mining and Geology to the Glasgow and West of Scotland Technical College.

Units of Measurement, Conductors, &c.—The Theory of the Dynamo.—The Dynamo, Details of Construction and Working.—Motors.—Lighting Installations in Collieries.—Pumping by Electricity.—Electrical Haulage.—Coal Cutting.—Miscellaneous Applications of Electricity in Mines.—Coal Mines Regulation Act (Electricity).—INDEX.

"A clear and concise introduction to electrical practice in collieries."—*Mining Journal*.

In Crown 8vo. Handsome Cloth. 8s. 6d. net.

MINING LAW OF THE BRITISH EMPIRE.

By CHARLES J. ALFORD, F.G.S., M. Inst. M.M.

CONTENTS.—The Principles of Mining Law.—The Mining Law of Great Britain.—British India.—Ceylon.—Burma.—The Malay Peninsula.—British North Borneo.—Egypt.—Cyprus.—The Dominion of Canada.—British Guiana.—The Gold Coast Colony and Ashanti.—Cape of Good Hope.—Natal.—Orange River Colony.—Transvaal Colony.—Rhodesia.—The Commonwealth of Australia.—New Zealand, &c.—INDEX.

"Cannot fail to be useful . . . we cordially recommend the book."—*Mining World*.

SEVENTH EDITION. In Large 8vo. Price 10s. 6d.

MINE ACCOUNTS AND MINING BOOK-KEEPING.

For Students, Managers, Secretaries, and others.

With Examples taken from Actual Practice of Leading Companies.

By JAMES GUNSON LAWN, A.R.S.M., A.M. Inst. C.E., F.G.S.,
Head of the Mining Department, Camborne School of Mines.

EDITED BY SIR C. LE NEVE FOSTER, D.Sc., F.R.S.

"It seems impossible to suggest how Mr. LAWN's book could be made more COMPLETE or more VALUABLE, careful, and exhaustive."—*Accountants' Magazine*.

THIRD EDITION. In Pocket Size, Strongly Bound in Leather, 3s. 6d.

Provided with Detachable Blank Pages for MS.

**THE MINING ENGINEERS' REPORT BOOK
AND DIRECTORS' AND SHAREHOLDERS' GUIDE TO MINING REPORTS.**

By EDWIN R. FIELD, M. INST. M.M.

With Notes on the Valuation of Property, and Tabulating Reports,
Useful Tables, and Examples of Calculations, &c.

"AN ADMIRABLY compiled book which Mining Engineers and Managers will find EXTREMELY USEFUL."—*Mining Journal*.

In Crown 8vo. Handsome Cloth. Illustrated. 10s. 6d. net.

**A DICTIONARY OF
SPANISH-ENGLISH AND SPANISH-AMERICAN MINING,
METALLURGICAL, AND ALLIED TERMS.**

To which some Portuguese and Portuguese-American (Brazilian) Terms are added.

By EDWARD HALSE, A.R.S.M.,

Mem. Inst. Min. and Metall., of the Eng. Inst. of Min. and Metall. Engrs., &c., &c

"Will be found of the greatest service to the mining profession."—*Mining Journal*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS ON SINKING, EXPLOSIVES, &c.

In Medium 8vo, Handsome Cloth. With 18 Figures in the Text,
and 19 Folding Plates. 10s. 6d. net.

SHAFT-SINKING IN DIFFICULT CASES.

By J. RIEMER,

TRANSLATED BY J. W. BROUGH, A.M. INST. C.E.

CONTENTS.—Shaft Sinking by Hand.—Shaft Sinking by Boring.—The Freezing Method.—The Sinking Drum Process.—BIBLIOGRAPHY.—INDEX.

"The translator deserves the thanks of the mining community for placing this valuable work before them. . . . The work is one which every mining engineer should include in his library."—*Mining World*.

SECOND EDITION, Revised. In Large 8vo, with Numerous Illustrations
and Folding Plates. 10s. 6d.

BLASTING: AND THE USE OF EXPLOSIVES.

By OSCAR GUTTMANN, M. INST. C.E., F.I.C., F.C.S.

CONTENTS.—Historical Sketch.—Blasting Materials.—Qualities and Handling of Explosives.—The Choice of Blasting Materials.—Preparation of Blasts.—Chamber Mines.—Charging of Boreholes.—Determination of Charge.—Blasting in Boreholes.—Firing.—Results of Working.—Various Blasting Operations.—INDEX.

"Should prove a *volume-mesum* to Mining Engineers and all engaged in practical work"
—*Iron and Coal Trades Review*.

In Medium 8vo, Cloth. With many Illustrations in the Text.
Four Full Page Plates and Four Folding Tables. 6s. net.

**NEW METHODS OF
TESTING EXPLOSIVES.**

By O. E. BICHEL.

TRANSLATED AND EDITED BY ALEX. LARSEN, M. INST. C.E.

CONTENTS.—Introductory.—Historical.—Testing Stations.—Power Gauges.—Products of Combustion.—Rate of Detonation.—Length and Duration of Flame.—After-Flame Ratio.—Transmission of Explosion.—Conclusions.—Efficiency.

"Its pages bristle with suggestions and actual experimental results to an extent seldom found in a volume of five times its size."—*Arms and Explosives*.

In Crown 8vo. Handsome Cloth. Fully Illustrated.

**A MANUAL ON
ELECTRICAL SIGNALLING IN MINES.**

By GERALD J. HOOGHWINKEL, M. INST. E.E., M.I. MIN. E.

CONTENTS.—SECTION I.—Electric Haulage Signals—(a) Acoustic Signals.—(b) Optical Signals.—(c) Acoustic Optical Signals.—Current Supply.—Batteries.—Accumulators.—Main Supply.—Design and Construction of Signalling Installations.—Maintenance of Signalling Installations. SECTION II.—Electric Shaft Signals—(a) Acoustic Signals.—(b) Electro-Mechanical Signals.—(c) Optical Acoustic Signals.—Signals for Winding Minerals.—For Winding Men.—Signalling from the Cage.—Emergency Signals.—Bells.—Mine Telegraphs.—Mine Telephones. SECTION III.—Special Applications in Mines.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

SECOND EDITION, Revised Throughout. In Medium 8vo. With
Numerous Plates, Maps, and Illustrations. 21s. net.

CYANIDING GOLD & SILVER ORES.

A Practical Treatise on the Cyanide Process; its Application,
Methods of Working, Design and Construction of
Plant, and Costs.

By H. FORBES JULIAN,

Mining and Metallurgical Engineer; Specialist in Gold; Late Technical Adviser of the
Deutsche Gold und Silber Scheide Anstalt, Frankfurt-on-Main.

AND EDGAR SMART, A.M.I.C.E.,

Civil and Metallurgical Engineer.

"A handsome volume of 400 pages which will be a valuable book of reference for all
associated with the process."—*Mining Journal*.

"The authors are to be congratulated upon the production of what should prove to be
standard work."—*Page's Magazine*.

In Large Crown 8vo. With 13 Plates and many Illustrations in the Text.
Handsome Cloth. 7s. 6d. net.

THE CYANIDE PROCESS OF GOLD EXTRACTION.

A Text-Book for the Use of Metallurgists and Students at
Schools of Mines, &c.

By JAMES PARK, F.G.S., M.INST.M.M.,

Professor of Mining and Director of the Otago University School of Mines; late Director
Thames School of Mines, and Geological Surveyor and Mining Geologist
to the Government of New Zealand.

FOURTH ENGLISH EDITION. Thoroughly Revised and Greatly Enlarged.
With additional details concerning the Siemens-Halske and other
recent processes.

"Deserves to be ranked as amongst the BEST OF EXISTING TREATISES."—*Mining Journal*.

THIRD EDITION, Revised. With Plates and Illustrations. Cloth, 3s. 6d.

GETTING GOLD:

A GOLD-MINING HANDBOOK FOR PRACTICAL MEN.

By J. C. F. JOHNSON, F.G.S., A.I.M.E.,

Life Member Australasian Mine-Managers' Association.

GENERAL CONTENTS.—Introductory: Prospecting (Alluvial and General)—
Lode or Reef Prospecting—Genesis of Gold—Auriferous Lodes—Drifts—
Gold Extraction—Lixivation—Calcination—Motor Power and its Transmission
Company Formation—Mining Appliances and Methods—Australasian
Mining Regulations.

"PRACTICAL from beginning to end . . . deals thoroughly with the Prospecting,
Sinking, Crushing, and Extraction of gold."—*Brit. Australasian*.

In Crown 8vo. Illustrated. Fancy Cloth Boards. 4s. 6d.

GOLD SEEKING IN SOUTH AFRICA:

A Handbook of Hints for intending Explorers, Prospectors,
and Settlers.

By THEO KASSNER,

Mine Manager, Author of the Geological Sketch Map of the De Kaap Gold Fields.

With a Chapter on the Agricultural Prospects of South Africa.

"As fascinating as anything ever penned by Jules Verne."—*African Commerce*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

GRIFFIN'S "NEW LAND" SERIES.

Practical Hand-Books for the Use of Prospectors, Explorers, Settlers, Colonists, and all Interest-ed in the opening up and Development of New Lands.

EDITED BY GRENVILLE A. J. COLE, M.R.I.A., F.G.S.,
Professor of Geology in the Royal College of Science for Ireland, and Examiner in the University of London.

*In Crown 8vo. Handsome Cloth. 5s.
With Numerous Maps Specially Drawn and Executed for this Work.*

NEW LANDS: THEIR RESOURCES AND PROSPECTIVE ADVANTAGES.

By HUGH ROBERT MILL, D.Sc., LL.D., F.R.S.E.,

"A want admirably supplied. . . . Has the advantage of being written by a pro-
fessed Geographer."—*Geographical Journal*.

With many Engravings and Photographs. Handsome Cloth, 4s. 6d.

FOOD SUPPLY.

By ROBERT BRUCE,

Agricultural Superintendent to the Royal Dublin Society.

With Appendix on Preserved Foods by C. A. MITCHELL, B.A., F.L.C.

"The work is one which will appeal to those intending to become farmers at home or in the Colonies, and who desire to obtain a general idea of the true principles of farming in ALL ITS BRANCHES."—*Journal of the Royal Colonial Inst.*

SIXTH EDITION. *With Illustrations. Handsome Cloth, 5s.*

PROSPECTING FOR MINERALS.

A Practical Handbook for Prospectors, Explorers, Settlers, and all interested in the Opening up and Development of New Lands.

By S. HERBERT COX, Assoc.R.S.M., M.Inst.M.M., F.G.S.,

Professor of Mining at the Royal School of Mines.

GENERAL CONTENTS.—Introduction and Hints on Geology—The Determination of Minerals: Use of the Blow-pipe, &c.—Rock forming Minerals and Non-Metallic Minerals of Commercial Value: Rock Salt, Borax, Marbles, Lithographic Stone, Quartz and Opal, &c., &c.—Precious Stones and Gems—Stratified Deposits: Coal and Ores—Mineral Veins and Lodes—Irregular Deposits—Dynamics of Lodes: Faults, &c.—Alluvial Deposits—Noble Metals: Gold, Platinum, Silver, &c.—Lead—Mercury—Copper—Tin—Zinc—Iron—Nickel &c.—Sulphur, Antimony, Arsenic, &c.—Combustible Minerals—Petroleum—General Hints on Prospecting—Glossary—Index.

"This ADMIRABLE LITTLE WORK . . . written with SCIENTIFIC ACCURACY in a CLEAR and LUCID style. . . . AN IMPORTANT ADDITION to technical literature."
—*Mining Journal*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

Demy 8vo. Handsome cloth, 34s

Stratigraphical Geology & Palæontology,

ON THE BASIS OF PHILLIPS.

By ROBERT ETHERIDGE, F.R.S.,

OF THE NATURAL HIST. DEPARTMENT, BRITISH MUSEUM, LATE PALÆONTOLOGIST TO THE GEOLOGICAL SURVEY OF GREAT BRITAIN, PAST PRESIDENT OF THE GEOLOGICAL SOCIETY, ETC.

With Map, Numerous Tables, and Thirty-six Plates.

" . . . Must take HIGH RANK AMONG WORKS OF REFERENCE."—*Athenæum*.

In Crown 8vo. Fully Illustrated. Cloth. 10s. 6d. net.

GEOLOGY FOR ENGINEERS.

By LIEUT.-COL. SORSBIE, R.E.

CONTENTS.—Dynamical and Structural Geology.—Rocks and Minerals.—Historical Geology.—Geological Observation.—Practical Geology.—Coast Erosion.—INDEX.

"Should be in the possession of every engineer."—*Mining World*.

In Crown 8vo. Handsome Cloth. 3s. net.

A BIBLIOGRAPHY OF THE MINERAL WEALTH AND GEOLOGY OF CHINA.

By C. Y. WANG, M.A., B.Sc., M. Am. Inst. Min. Eng., M. Iron & Steel Inst

SIXTH EDITION, Thoroughly Revised. With Illustrations. Cloth. 10s. 6d.

AIDS IN PRACTICAL GEOLOGY:

WITH A SECTION ON PALÆONTOLOGY.

By PROFESSOR GRENVILLE COLE, M.R.I.A., F.G.S.

GENERAL CONTENTS.—

Part I.—Sampling of Earth's Crust. | Part III.—Examination of Rocks.
Part II.—Examination of Minerals. | Part IV.—Examination of Fossils.

"That the work deserves its title, that it is full of 'Aids,' and in the highest degree PRACTICAL," will be the verdict of all who use it."—*Nature*.

OPEN-AIR STUDIES IN GEOLOGY.

By PROF. G. COLE.

[See p. 73.]

In Crown 8vo. Handsome Cloth. 2s. 6d.

RESEARCHES on the PAST and PRESENT HISTORY of THE EARTH'S ATMOSPHERE.

Including the latest Discoveries and their Practical Applications.

By DR. THOMAS LAMB PHIPSON.

"The book should prove of interest to general readers, as well as to meteorologists and other students of science."—*Nature*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Griffin's Metallurgical Series.

STANDARD WORKS OF REFERENCE

FOR

Metallurgists, Mine-Owners, Assayers, Manufacturers,
and all interested in the development of
the Metallurgical Industries.

EDITED BY

Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

In Large 8vo. Handsome Cloth With Illustrations.

INTRODUCTION to the **STUDY** of **METALLURGY.**

By the EDITOR. SIXTH EDITION. (See p. 48.)

GOLD (The Metallurgy of). By THOS. KIRKE ROSE, D.Sc., Assoc. R.S.M., F.C.S., Chemist and Assayer of the Royal Mint. FIFTH EDITION. 21s. (See p. 48.)

LEAD (The Metallurgy of). By H. F. COLLINS, Assoc. R.S.M., M.Inst.M.M. SECOND EDITION. (See p. 49.)

SILVER (The Metallurgy of). By H. F. COLLINS, A.R.S.M., M.Inst.M.M. SECOND EDITION. (See p. 49.)

IRON (The Metallurgy of). By T. TURNER, A.R.S.M., F.I.C., F.C.S. THIRD EDITION, Revised. 16s. net. (See p. 50.)

STEEL (The Metallurgy of). By F. W. HARBORD, Assoc.R.S.M., F.I.C., and J. W. HALL, A.M.Inst.C.E. FOURTH EDITION. In Two Volumes. Profusely Illustrated. (See p. 50.)

ALLOYS. By EDWARD F. LAW, Assoc.R.S.M. With Frontispiece in Colours, and Fine Series of Micro-photographs. 12s. 6d. net. (See p. 49.)

ANTIMONY. By C. Y. WANG, M.A., B.Sc. Fully Illustrated. 12s. 6d. net. (See p. 50.)

Will be Published at Short Intervals.

METALLURGICAL MACHINERY: the Application of Engineering to Metallurgical Problems. By HENRY CHARLES JENKINS, Wh.Sc., Assoc. R.S.M.

COPPER (The Metallurgy of). By THOS. C. CLOUD, Assoc. R.S.M.

. Other Volumes in Preparation.

LONDON: CHARLES GRIFFIN & CO., LIMITED EXETER STREET, STRAND.

GRIFFIN'S METALLURGICAL SERIES.

SIXTH EDITION, thoroughly Revised and considerably Enlarged. Large 8vo, Pp. i-xv + 478. With numerous Illustrations and Micro-Photographic Plates of different varieties of Steel. 18s. net.

An Introduction to the Study of
METALLURGY.

BY

Sir W. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S., A.R.S.M.,
Late Chemist and Assayer of the Royal Mint, and Professor of Metallurgy
in the Royal College of Science.

Revised throughout by F. W. HARBORD, A. R. S. M., F. I. C.

GENERAL CONTENTS.—The Relation of Metallurgy to Chemistry.—Physical Properties of Metals.—Alloys. The Thermal Treatment of Metals.—Fuel and Thermal Measurements.—Materials and Products of Metallurgical Processes.—Furnaces.—Means of Supplying Air to Furnaces.—Thermo-Chemistry.—Typical Metallurgical Processes.—The Micro-Structure of Metals and Alloys.—Economic Considerations.

"No English text-book at all approaches this in the COMPLETENESS with which the most modern views on the subject are dealt with. Professor Austen's volumes will be INVALUABLE, not only to the student, but also to those whose knowledge of the art is far advanced."—*Chemical News*.

FIFTH EDITION, Revised, Considerably Enlarged, and in part Re-written.
With Frontispiece and numerous Illustrations. 21s.

THE METALLURGY OF GOLD.

BY

T. KIRKE ROSE, D.Sc.Lond., Assoc.R.S.M.
Chemist and Assayer of the Royal Mint.

GENERAL CONTENTS.—The Properties of Gold and its Alloys.—Chemistry of the Compounds of Gold.—Mode of Occurrence and Distribution of Gold.—Shallow Placer Deposits.—Deep Placer Deposits.—Quartz Crushing in the Stamp Battery.—Amalgamation in the Stamp Battery.—Other Forms of Crushing and Amalgamating Machinery.—Concentration in Gold Mills.—Dry Crushing.—Re-grinding.—Roasting.—Chlorination; The Plattner Process, The Barrel Process, The Vat-Solution Process.—The Cyanide Process.—Chemistry of the Cyanide Process.—Refining and Parting of Gold Bullion.—Assay of Gold Ores.—Assay of Gold Bullion.—Statistics of Gold Production.—Bibliography.—INDEX.

"A COMPREHENSIVE PRACTICAL TREATISE ON THIS IMPORTANT SUBJECT."—*The Times*.
"The most complete description of the chlorination process which has yet been published."—*Mining Journal*.

"Adapted for all who are interested in the Gold Mining Industry, being free from technicalities as far as possible, but is more particularly of value to those engaged in the industry."—*Cape Times*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

GRIFFIN'S METALLURGICAL SERIES.

EDITED BY SIR W. ROBERTS-AUSTEN, K.C.B., F.R.S., D.C.L.
In Large Svo. Handsome Cloth. With Illustrations.

SECOND EDITION, Revised Throughout and Enlarged. Pp. i-xx + 538.
 With 314 Illustrations, including 12 Folding Plates. 21s. net.

THE METALLURGY OF LEAD.

By H. F. COLLINS, Assoc.R.S.M., M.INST.M.M.

CONTENTS.—INTRODUCTORY.—The Properties of Lead and its Principal Compounds.—Lead Ores.—LEAD SMELTING in Reverberatories.—Lead Smelting in Hearths.—Roasting Lead and Silver Ores.—Blast-Roasting of Lead Ores.—Blast-Furnace Lead Smelting: Principles, Plant, Practice, Products, Examples, Costs and Losses, Ore Purchasing.—Fine-Dust: Composition, Collection, and Treatment.—DESILVERISATION.—Softening and Refining for Market.—Parkinson Process.—Parkes Process.—Cupellation and Refining.—Electrolytic Refining.—SUPPLEMENTARY: Works Assaying and Analytical Methods.—Zinc-Lead Sulphides.—Flotation Processes.—INDEX.

"A THOROUGHLY SOUND and useful digest. May with EVERY CONFIDENCE be recommended."—*Mining Journal*.

SECOND EDITION, Revised Throughout and Enlarged. In Preparation.

THE METALLURGY OF SILVER.

By H. F. COLLINS, Assoc.R.S.M., M.INST.M.M.

Comprising Details regarding the Sources and Treatment of Silver Ores, together with Descriptions of Plant, Machinery, and Processes of Manufacture, Refining of Bullion, Cost of Working, &c.

"The author has focused a LARGE AMOUNT OF VALUABLE INFORMATION into a convenient form. . . . The author has evidently considerable practical experience, and describes the various processes clearly and well."—*Mining Journal*.

Frontispiece in Colours, and Beautiful Series of Photo-micrographs.
 12s. 6d. net.

ALLOYS
AND THEIR INDUSTRIAL APPLICATIONS.

By EDWARD F. LAW, A.R.S.M.

CONTENTS.—Introduction.—Properties of Alloys.—Methods of Investigation.—Constitution.—Influence of Temperature on Properties.—Corrosion of Alloys.—Copper Alloys, Brass, Bronzes.—Special Brasses and Bronzes.—German Silver and Miscellaneous Copper Alloys.—White Metal Alloys.—Anti-Friction Alloys.—Aluminium Alloy.—Silver and Gold Alloys.—Iron Alloys.—Miscellaneous Alloys (Amalgams, &c.).—INDEX.

"Concise and practical . . . a valuable amount of information that will be appreciated by student and manufacturer alike."—*Foundry Trades' Journal*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

GRIFFIN'S METALLURGICAL SERIES.

FOURTH EDITION, Thoroughly Revised Throughout. With Numerous Illustrations. Large 8vo. Two Volumes, Handsome Cloth. 36s. net.

With Additional Chapter on The Electric Smelting of Steel.

THE METALLURGY OF STEEL.

BY F. W. HARBORD, ASSOC.R.S.M., F.I.C.,

AND J. W. HALL, A.M.INST.C.E.

Vol. I.—Metallurgy.

Vol. II.—Mechanical Treatment.

(N.B.—These Volumes are not Sold Separately.)

ABRIDGED CONTENTS.—The Plant, Machinery, Methods and Chemistry of the Bessemer and of the Open Hearth Processes (Acid and Basic).—The Influence of Metalloids, Heat Treatment, Special Steels, Microstructure, Testing, and Specifications.—The Mechanical Treatment of Steel comprising Mill Practice, Plant and Machinery.

The Engineer says, at the conclusion of a review of this book—"We cannot conclude without earnestly recommending all who may be interested as makers or users of steel, which practically means the whole of the engineering profession, to make themselves acquainted with it as speedily as possible, and this may be the more easily done as the published price, considering the size of the book, is extremely moderate."

THIRD EDITION, Revised and Enlarged. With many new Plates.
16s. net.

THE METALLURGY OF IRON.

BY THOMAS TURNER ASSOC.R.S.M., F.I.C.,

Professor of Metallurgy in the University of Birmingham.

General Contents.—Early History of Iron.—Modern History of Iron.—The Age of Steel.—Chief Iron Ores.—Preparation of Iron Ores.—The Blast Furnace.—The Air used in the Blast Furnace.—Reactions of the Blast Furnace.—The Gaseous Products of the Blast Furnace.—The Fuel used in the Blast Furnace.—Slags and Fluxes of Iron Smelting.—Properties of Cast Iron.—Foundry Practice.—Wrought Iron.—Indirect Production of Wrought Iron.—The Puddling Process.—Further Treatment of Wrought Iron.—Corrosion of Iron and Steels.

"A THOROUGHLY USEFUL BOOK, which brings the subject UP TO DATE. OF GREAT VALUE to those engaged in the iron industry."—*Mining Journal*.

. For Professor Turner's *Lectures on Iron-Founding*, see page 53

In Large 8vo. Handsome Cloth. Fully Illustrated. 12s. 6d. net.

ANTIMONY:

Its History, Chemistry, Mineralogy, Geology, Metallurgy, Uses and Preparation, Analysis, Production and Valuation.

By C. Y. WANG, M.A., B.Sc.,

Mem. Am. Inst. Mining Eng.; Mem. Iron and Steel Institute; Geologist for the Quang Si Province, China, &c., &c.

"A book which stands alone, inasmuch as there is not, to our knowledge, any other complete treatise on antimony among all the English text-books."—*Iron and Coal Trades' Review*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

In Medium 8vo. Handsome Cloth. Profusely Illustrated.

LECTURES ON MODERN COPPER SMELTING

By DONALD M. LEVY, M.Sc., A.R.S.M.,

Assistant Lecturer in Metallurgy University of Birmingham

ADDED CONTENTS.—Historical.—Price and Cost of Production and Statistics.—Uses of Copper as Metal and Alloy.—Effect of Impurities.—Compounds.—Ores.—Preliminary Treatment.—Smelting.—Reverberatory Smelting Practice.— blast Furnace Practice.—Bessemerising of Copper Mattes.—Purification and Refining of Crude Copper.—INDEX.

In Medium 8vo. Handsome Cloth. With Illustrations. 10s. 6d. net.

CAST IRON

IN THE LIGHT OF RECENT RESEARCH.

By W. H. HATFIELD, B.Met., A.M.I.Mech.E.

CONTENTS.—INTRODUCTION.—Cast Iron from the Standpoint of the Equilibrium Diagram of the Non-carbon System.—Influences of Silicon.—Of Phosphorus.—Of Sulphur.—Of Manganese.—Of Other Elements.—Of Casting Temperature.—Shrinkage and Contraction.—Growth of Cast Iron under Repeated Heatings.—Effect of Superheated Steam.—Malleable Cast Iron.—Heat Treatment of Cast Iron.—Decarburisation of White Cast-iron Castings.—Mechanical Properties of Cast and Malleable Cast Iron.—Slags.—APPENDICES.—INDEX.

TWELFTH EDITION. With Tables and Illustrations. Cloth, 10s. 6d.

A TEXT-BOOK OF ASSAYING:

For the use of Students, Mine Managers, Assayers, &c.

By J. J. BERINGER, F.I.C., F.C.S.,

Public Analyst for, and Lecturer to the Mining Association of, Cornwall.

AND C. BERINGER, F.C.S.,

Late Chief Assayer to the Rio Tinto Copper Company, London.

GENERAL CONTENTS.—PART I.—INTRODUCTORY: MANIPULATION: Sampling; Drying; Calculation of Results—Laboratory-books and Reports. METHODS: Dry Gravimetric; Wet Gravimetric—Volumetric Assays; Titrimetric, Colorimetric, Gasometric—Weighing and Measuring—Reagents—Formulae, Equations, &c.—Specific Gravity.

PART II.—METALS: Detection and Assay of Silver, Gold, Platinum, Mercury, Copper, Lead, Thallium, Bismuth, Antimony, Iron, Nickel, Cobalt, Zinc, Cadmium, Tin, Tungsten, Titanium, Manganese, Chromium, &c.—Earths, Alkalies.

PART III.—NON-METALS: Oxygen and Oxides; The Halogens—Sulphur and Sulphates—Arsenic, Phosphorus, Nitrogen—Silicon, Carbon, Boron—Useful Tables.

"A REALLY MERITORIOUS WORK, that may be safely depended upon either for systematic instruction or for reference."—*Nature*.

Large 8vo. Cloth. With Illustrations. 12s. 6d. net.

METALLURGICAL ANALYSIS & ASSAYING:

A THREE YEARS' COURSE FOR STUDENTS OF SCHOOLS OF MINES.

By W. A. MACLEOD, B.A., B.Sc., AND CHAS. WALKER, F.C.S.

"The publication of this volume tends to prove that the teaching of metallurgical analysis and assaying in Australia rests in competent hands."—*Nature*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

VOL. I. NOW READY.

In Handsome Cloth, Leather Back. Price 21s. net.

RAND METALLURGICAL PRACTICE.**VOLUME I. contains—**

Introduction by RALPH STOKES.

Breaking and Sorting—Sand Treatment, by J. E. THOMAS, A.I.M.M., &c.

Stamp Milling, by G. O. SMART, A.I.M.M., &c.

Tube Milling: Slime Treatment, by W. R. DOWLING, M.I.M.M., &c.

Slime Treatment, by H. A. WHITE, Mem. Council of C.M. and M. Soc. S.A.

Precipitation: Clean-up and Smelting, by E. H. JOHNSON, M.I.M.M., &c.

Chemistry of Basket Ore Treatment, by W. A. CALDECOTT, D.Sc., F.C.S.,

F.R.S., &c.

Assaying, Testing, by A. McA. JOHNSTON, M.A., M.I.M.M., F.C.S., &c.

RAND METALLURGICAL PRACTICE.**VOLUME II. contains—**

Design and Construction of Plant, Transport of Materials, by C. O.

SCHMITT, M.I.M.M., Member Council of Transvaal Institution of
Mechanical Engineers.

In Crown 8vo. Handsome Cloth. Fully Illustrated. 3s. net.

AN INTRODUCTION TO**PRACTICAL METALLURGY.**

By PROF. THOMAS TURNER, A.R.S.M., F.I.C.

"It is an excellent and handy book for its purpose, and will have a far wider range of usefulness than for class work alone."—*Practical Engineer*.

FOURTH EDITION, Revised. With Numerous Illustrations. 6s.

A TEXT-BOOK OF**ELEMENTARY METALLURGY.**

Including the Author's PRACTICAL LABORATORY COURSE.

By A. HUMBOLDT SEXTON, F.I.C., F.O.S.

"Just the kind of work for Students COMMENCING the study of Metallurgy, or for ENGINEERING Students."—*Practical Engineer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

- In Crown 8vo. Handsome cloth. With 102 Illustrations. 6s. net.

A HANDBOOK ON
METALLIC ALLOYS:
 Their Structure and Constitution.

By GILBERT H. GULLIVER, B.Sc., F.R.S.E.

„A valuable addition to existing literature on alloys.”—*Foundry Trades' Journal*.

In Large 8vo. Handsome Cloth. Price 4s.

QUANTITATIVE METALLURGICAL ANALYSIS.

TABLES FOR LABORATORY USE.

ON THE PRINCIPLE OF "GROUP" SEPARATIONS.

By J. JAMES MORGAN, F.C.S., M.S.C.I.

“The Author may be congratulated on the way his work has been carried out.”—*The Engineer*

THIRD EDITION. In Handsome Cloth. Revised, Enlarged, and Re-written. Pp. i-xv + 425. Fully Illustrated. 12s. 6d. net.

A TREATISE ON

ELECTRO-METALLURGY:

Embracing the Application of Electrolysis to the Plating, Depositing, Smelting, and Refining of various Metals, and to the Reproduction of Printing Surfaces and Art-Work, &c.

By W. G. McMILLAN, F.J.C., and W. R. COOPER, M.A., B.Sc.

CONTENTS.—Introductory and Historical.—Theoretical and General.—Sources of Current.—General Conditions to be Observed in Electro-Plating.—Plating Adjuncts and Deposition of Plant.—The Cleansing and Preparation of Work for the Depositing-Vat, and subsequent Plating of Plated Goods.—The Electro-deposition of Copper.—Electrotyping.—The Electro-deposition of Silver, Gold, Nickel and Cobalt, Iron, Platinum, Zinc, Chromium, Cadmium, Tin, Lead, Antimony, Bismuth, and Palladium; Electrochromy.—The Electro-deposition of Alloys.—Electro-metallurgical Extraction and Refining Processes.—The Recovery of certain Metals from their Solutions or from Waste Substances.—The Determination of the Proportion of Metal in certain Depositing Solutions.—Power required for Electrolytic Work.—Modern Theories of Electrolysis.—Glossary.—Addenda.—INDEX.

“A most valuable cyclopaedia as well as a guiding text-book . . . gives a wonderful amount of information.”—*Metal Industry*.

SECOND EDITION, Thoroughly Revised and Enlarged. In large 8vo. With Numerous Illustrations and Three Folding-Plates. 21s. net.

ELECTRIC SMELTING & REFINING:

A Practical Manual of the Extraction and Treatment of Metals by Electrical Methods.

Being the “ELEKTRO-METALLURGIE” of DR. W. BORCHERS.

Translated from the Latest German Edition by WALTER G. McMILLAN, F.I.C., F.C.S.

“COMPREHENSIVE and AUTHORITATIVE . . . not only FULL of VALUABLE INFORMATION, but gives evidence of a THOROUGH INSIGHT into the technical VALUE and POSSIBILITIES of all the methods discussed.”—*The Electrician*.

LONDON: CHARLES GRIFFIN & CO., LIMITED EXETER STREET, STRAND.

SECOND EDITION. In Medium Svo. Handsome Cloth. Fully Illustrated.

GENERAL FOUNDRY PRACTICE:

*A Practical Handbook for Iron, Steel and Brass Founders,
Metallurgists, and Students of Metallurgy.*

By A. McWILLIAM, A.R.S.M., AND PERCY LONGMUIR,

"The student of foundry work . . . needs no other text-book. . . . The book contains a tremendous amount of information, and is well written."—*Engineering Times.*

SECOND EDITION. Extra Crown Svo. With many Illustrations.
3s. 6d. net.

LECTURES ON IRON-FOUNDING.

By THOMAS TURNER, M.Sc., A.R.S.M., F.I.C.,

Professor of Metallurgy in the University of Birmingham.

CONTENTS.—Varieties of Iron and Steel.—Application of Cast Iron.—History.—Production.—Iron Ores.—Composition.—The Blast Furnace.—Materials.—Reactions.—Grading Pig Iron.—Carbon, Silicon, Sulphur, Phosphorus, Manganese, Aluminium, Arsenic, Copper, and Titanium.—The Foundry.—General Arrangement.—Re-melting Cast Iron.—The Cupola.—Fuel Used.—Changes due to Re-melting.—Moulds and Moulding.—Foundry Ladles.—Pouring and Pouring Temperature.—Common Troubles.—Influence of Shape and Size on Strength of Castings.—Tests
"Ironfounders will find much information in the book."—*Iron Trade Circular England's*).

In Crown Svo. Handsome Cloth. 7s. 6d. net.

BLAST FURNACE PRACTICE.

By J. JAMES MORGAN, F.C.S., M.S.C.I.,

Author of "Quantitative Metallurgical Tables." &c.

CONTENTS.—Requirements.—Iron Ores.—Fuel.—Flux.—Slags.—Quantity of Slag.—Burden, Charge, Round.—The Blast.—Ore Mixing.—Amount and Composition of the Iron.—Calculation of Flux.—Heating the Blast.—Stoves—Drying, Charging, and Cleaning.—Drying the Furnace.—Filling the Furnace, and Lighting.—Charging the Furnace.—Descent of the Charge.—Flushing.—Tapping.—Hard Tapping Hole.—Running down the Beds (Casting).—Judging the Temperature.—Controlling the Temperature.—Temperature and the Reduction of Silicon.—The Pig Iron.—Fuel Consumption.—Economy in Fuel Consumption.—Tuyeres: Leaky, Changing.—Cooler or "Jumbo."—Obstructions.—Pillaring.—Breakouts.—Hot Spots.—Scaffolds (Hanging).—Slips.—Bumping Down.—Blowing Out.—INDEX.

"Excellent. . . . It is essentially suitable for the practical man, and to the beginner particularly it should prove valuable."—*Iron and Coal Trades Record.*

SECOND EDITION, Revised. In Demy Svo. With 145 Illustrations
and 12 new Plates. 7s. 6d. net.

THE ART OF THE GOLDSMITH AND JEWELLER.

*A Manual on the Manipulation of Gold and the
Manufacture of Personal Ornaments.*

By THOS. B. WIGLEY,

Headmaster of the Jewellers and Silversmiths' Assoc. Tech. School, Birmingham.

ASSISTED BY J. H. STANSBIE, B.Sc. (LOND.), F.I.C.,

Lecturer at the Birmingham Municipal Technical School.

"A recognised standard work."—*Jewellers' and Watchmakers' Trade Advertiser.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION, Revised, Enlarged, and Re-set Throughout on Larger Page.
With Valuable Bibliography, New Maps, Illustrations, &c. 45s net.

IN TWO VOLUMES.
A TREATISE ON

PETROLEUM.

By SIR BOVERTON REDWOOD,
D.Sc., F.R.S.E., Assoc. Inst. C.E., F.I.C.

CONTENTS.—SECTION I.: Historical Account of the Petroleum Industry.—SECTION II.: Geological and Geographical Distribution of Petroleum and Natural Gas.—SECTION III.: The Chemical and Physical Properties of Petroleum and Natural Gas.—SECTION IV.: The Origin of Petroleum and Natural Gas.—SECTION V.: The Production of Petroleum, Natural Gas, and Ozokerite.—SECTION VI.: The Refining of Petroleum.—SECTION VII.: The Shale Oil and Allied Industries.—SECTION VIII.: The Transport, Storage, and Distribution of Petroleum.—SECTION IX.: The Testing of Crude Petroleum, Petroleum and Shale Oil Products, Ozokerite, and Asphalt.—SECTION X.: The Uses of Petroleum and its Products.—SECTION XI.: Statutory, Municipal, and other Regulations relating to the Testing, Storage, Transport, and Use of Petroleum and its Products.—APPENDICES.—BIBLIOGRAPHY.—INDEX.

"It is indisputably the most comprehensive and complete treatise on petroleum, and this statement is true, no matter on what branch of the industry a test of its merits is made. It is the only book in existence which gives the oil man a clear and reliable outline of the growth and present-day condition of the entire petroleum world. . . . There is a wonderfully complete collection of plates and illustrations."—*Petroleum World*.

SECOND EDITION, Revised. With Illustrations. Price 8s. 6d. net.

A HANDBOOK ON PETROLEUM FOR INSPECTORS UNDER THE PETROLEUM ACTS.

And for those engaged in the Storage, Transport, Distribution, and Industrial Use of Petroleum and its Products, and of Calcium Carbide. With suggestions on the Construction and Use of Mineral Oil Lamps.

By CAPTAIN J. H. THOMSON,

H.M. Chief Inspector of Explosives.

AND SIR BOVERTON REDWOOD,

Author of "A Treatise on Petroleum."

"A volume that will enrich the world's petroleum literature, and render a service to the British branch of the industry. . . . Reliable, indispensable, a brilliant contribution."—*Petroleum*.

SECOND EDITION, Revised. In Crown 8vo. Fully Illustrated.

THE LABORATORY BOOK OF MINERAL OIL TESTING.

By J. A. HICKS,

Chemist to Sir Bovertou Redwood.

Should be on the shelves of every analytical chemist in practice."—*Chemical Trade Journal*

SECOND EDITION. In Large Crown 8vo. Cloth. Fully Illustrated 6s. net.

OIL FUEL: ITS SUPPLY, COMPOSITION, AND APPLICATION.

By SIDNEY H. NORTH,

THOROUGHLY REVISED AND ENLARGED BY ED. BUTLER, M.I.MECH.E.

CONTENTS.—The Sources of Supply.—Economic Aspect of Liquid Fuel.—Chemical Composition of Fuel Oils.—Conditions of Combustion in Oil Fuel Furnaces.—Early Methods and Experiments.—Modern Burners and Methods.—Oil Fuel for Marine Purposes.—For Naval Purposes.—On Locomotives.—For Metallurgical and other Purposes.—Appendices.—INDEX.

"Everyone interested in this important question will welcome Mr. North's excellent text-book."—*Nature*.

THE PETROLEUM LAMP: Its Choice and Use. A Guide to the Safe Employment of the Paraffin Lamp. By CAPT. J. H. THOMSON and Sir BOVERTON REDWOOD. Illustrated. 1s. net.

"A work which will meet every purpose for which it has been written."—*Petroleum*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

In Two Vols., Large 8vo. With Illustrations. Sold Separately.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS.

BY

BERTRAM BLOUNT, F.I.C., & A. G. BLOXAM, F.I.C.

VOLUME I.—Chemistry of Engineering, Building, and Metallurgy.—General Contents.—INTRODUCTION.—Chemistry of the Chief Materials of Construction.—Sources of Energy.—Chemistry of Steam-raising.—Chemistry of Lubrication and Lubricants.—Metallurgical Processes used in the Winning and Manufacture of Metals. SECOND EDITION. 14s.

VOLUME II.—The Chemistry of Manufacturing Processes.—General Contents.—Sulphuric Acid Manufacture.—Alkali, &c.—Destructive Distillation.—Artificial Manure.—Petroleum.—Lime and Cements.—Clay and Glass.—Sugar and Starch.—Brewing and Distilling.—Oils, Resins, and Varnishes.—Soap and Candles.—Textiles and Bleaching.—Colouring Matters, Dyeing and Printing.—Paper and Pasteboard.—Pigments and Paints.—Leather, Glue, and Size.—Explosives and Matches.—Minor Manufactures. SECOND EDITION, Reprinted. Illustrated. 16s.

SECOND EDITION. In Large 8vo. Handsome Cloth. With 800 pages and 154 Illustrations. 25s. net.

OILS, FATS, BUTTERS, AND WAXES :

THEIR PREPARATION AND PROPERTIES, AND MANUFACTURE THEREFROM OF CANDLES, SOAPS, AND OTHER PRODUCTS.

By C. R. ALDER WRIGHT, D.Sc., F.R.S.,

Late Lecturer on Chemistry, St. Mary's Hospital Medical School; Examiner in "Soap" to the City and Guilds of London Institute.

Thoroughly Revised, Enlarged, and in Part Rewritten

By C. AINSWORTH MITCHELL, B.A., F.I.C., F.C.S.

"Will be found ABSOLUTELY INDISPENSABLE,"—*The Analyst*.

"Will rank as the STANDARD ENGLISH AUTHORITY ON OILS and FATS for many years to come."—*Industries and Iron*.

In Two Volumes, Half Morocco, each complete in itself.

PHYSICO-CHEMICAL TABLES

For the Use of Analysts, Physicians, Chemical Manufacturers and Scientific Chemists.

Volume I.—Chemical Engineering, Physical Chemistry.

Pp. i-xxvii + 54s. 24s. net.

Volume II.—Chemical Physics, Pure and Analytical Chemistry.

Pp. i-xiv + 549 to 1235. With Index to the two Volumes. 36s. net.

By JOHN CASTELL-EVANS, F.I.C., F.C.S.

The Work comprehends as far as possible ALL RULES and TABLES required by the Analyst, Brewer, Distiller, Acid- and Alkali-Manufacturer, &c., &c.; and also the principal data in THERMO-CHEMISTRY, ELECTRO-CHEMISTRY, and the various branches of CHEMICAL PHYSICS. Every possible care has been taken to ensure perfect accuracy, and to include the results of the most recent investigations.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SIXTH EDITION, Thoroughly Revised. Fully Illustrated. 21s.

FOODS: THEIR COMPOSITION AND ANALYSIS.

By A. WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S.,

Barrister-at-Law, Public Analyst for the County of Devon, and
Medical Officer of Health for St. Marylebone

AND M. WYNTER BLYTH, B.A., B.Sc., F.C.S.

GENERAL CONTENTS.—History of Adulteration.—Legislation.—Apparatus.—“Ash.”—Sugar.—Confectionery.—Honey.—Treacle.—Jams and Preserved Fruits.—Starches.—Wheaten-Flour.—Bread.—Oats.—Barley.—Rye.—Rice.—Maize.—Millet.—Potatoes.—Peas.—Lentils.—Beans.—Milk.—Cream.—Butter.—Oleo-Margarine.—Cheese.—Lard.—Tea.—Coffee.—Cocoa and Chocolate.—Alcohol.—Brandy.—Rum.—Whisky.—Gin.—Attack.—Liqueurs.—Absinthe.—Yeast.—Beer.—Wine.—Vinegar.—Lemon and Lime Juice.—Mustard.—Pepper.—Sweet and Bitter Almonds.—Annatto.—Olive Oil.—Water Analysis.—Appendix: Adulteration Acts, &c.

“A new edition of Mr. Wynter Blyth's Standard work, enriched with all the RECENT DISCOVERIES and IMPROVEMENTS, will be accepted as a boon.”—*Chemical News*.

FOURTH EDITION, Thoroughly Revised. In Large 8vo, Cloth, with
Tables and Illustrations. 21s. net.

POISONS: THEIR EFFECTS AND DETECTION.

By A. WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S.,

Barrister-at-Law, Public Analyst for the County of Devon, and
Medical Officer of Health for St. Marylebone.

GENERAL CONTENTS.—I.—Historical Introduction. II.—Classification—Statistics—Connection between Toxic Action and Chemical Composition—Life Tests—General Method of Procedure—The Spectroscope—Examination of Blood and Blood Stains. III.—Poisonous Cases. IV.—Acids and Alkalies. V.—More or less Volatile Poisonous Substances. VI.—Alkaloids and Poisonous Vegetable Principles. VII.—Poisons derived from Living or Dead Animal Substances. VIII.—The Oxalic Acid Group. IX.—Inorganic Poisons. Appendix: Treatment, by Antidotes or otherwise, of Cases of Poisoning.

“Undoubtedly THE MOST COMPLETE WORK on Toxicology in our language.”—*The Analyst*
“As a PRACTICAL GUIDE, we know no BETTER WORK.”—*The Lancet (on the Third Edition)*

Crown 8vo, Handsome Cloth. Fully Illustrated. 10s. 6d.

FLESH FOODS:

With Methods for their Chemical, Microscopical, and Bacteriological Examination.

A Practical Handbook for Medical Men, Analysts, Inspectors and others.

By C. AINSWORTH MITCHELL, B.A., F.I.C., F.C.S.

“A compilation which will be most useful for the class for whom it is intended.”—*A Chemist*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

SECOND EDITION. With Numerous Tables, Fully Illustrated.

DAIRY CHEMISTRY FOR DAIRY MANAGERS, CHEMISTS, AND ANALYSTS

A Practical Handbook for Dairy Chemists and others
having Control of Dairies.

By H. DROOP RICHMOND, F.I.C.,

CHEMIST TO THE AYLESBURY DAIRY COMPANY.

Contents.—I. Introductory.—The Constituents of Milk. II. The Analysis of Milk. III. Normal Milk: its Adulterations and Alterations, and their Detection. IV. The Chemical Control of the Dairy. V. Biological and Sanitary Matters. VI. Butter. VII. Other Milk Products. VIII. The Milk of Mammals other than the Cow.—Appendices.—Tables.—Index.

" . . . In our opinion the book is the BEST CONTRIBUTION ON THE SUBJECT THAT HAS YET APPEARED in the English language."—*Lancet* (on the First Edition).

In Crown 8vo, Fully Illustrated. 2s. 6d. net.

THE LABORATORY BOOK OF

DAIRY ANALYSIS.

By H. DROOP RICHMOND, F.I.C.,

Analyst to the Aylesbury Dairy Co., Ltd.

"Without doubt the best contribution to the literature of its subject that has ever been written."—*Medical Times*.

Fully Illustrated. With Photographs of Various Breeds of Cattle, &c.
6s. net.

MILK: ITS PRODUCTION & USES.

With Chapters on Dairy Farming, The Diseases of Cattle, and on the Hygiene and Control of Supplies.

By EDWARD F. WILLOUGHBY,

M.D. (Lond.), D.P.H. (Lond. and Camb.).

"We cordially recommend it to everyone who has anything at all to do with milk.
Dairy World.

In Large Crown 8vo. Cloth. Fully Illustrated. 4s. 6d. net.

ELEMENTARY AGRICULTURAL CHEMISTRY.

By HERBERT INGLE, B.Sc., F.I.C., F.C.S.

CONTENTS.—Introduction.—The Atmosphere.—The Soil—Natural Waters.—The Plant.—Manures.—Crops.—The Animal.—Foods and Feeding.—The Dairy.—Miscellaneous.—INDEX.

FIFTH EDITION. In Demy 8vo. Revised Throughout. Pp. i xi + 489.

With 101 Illustrations. In Cloth. 15s. net.

MICRO-ORGANISMS AND FERMENTATION.

By ALFRED JÖRGENSEN.

TRANSLATED BY SAMUEL H. DAVIES, M.Sc.

CONTENTS.—Microscopical and Physiological Investigations.—Biological Examination of Air and Water.—Bacteria.—Moulds.—Yeasts.—Pure Culture of Yeast on a large scale.—BIBLIOGRAPHY.—INDEX.

"The student taking up this subject would do well to work through this book first and then take Lefar's."—*Brewing Trade Review*

LONDON: CHARLES GRIFFIN & CO. LIMITED, FETTER STREET, STRAND.

• THIRD EDITION. In Handsome Cloth. Fully Illustrated. 21s. net.
PRINCIPLES AND PRACTICE OF BREWING.
 FOR THE USE OF STUDENTS AND PRACTICAL MEN.

By WALTER J. SYKES.

REVISED BY ARTHUR R. LING, F.I.C., F.C.S.,
 Editor of the Journal of the Institute of Brewing.

CONTENTS.—Physical Principles Involved.—The Chemistry of Brewing.—The Microscope.—Vegetable Biology.—Fermentation.—Water.—Barley and Mashing.—Arrangement of Brewery Plants.—Quantities of Materials.—Fermentation.—Antiseptics.—Finings.—Characteristics of Bees.—Diseases of Beer.—INDEX.

"A thorough and comprehensive text-book . . . up-to-date . . . a standard text-book."—*Brewers' Journal*.

In Large 8vo. Complete in Two Volumes.

Each Volume Complete in Itself, and Sold Separately.

TECHNICAL MYCOLOGY:

The Utilisation of Micro-organisms in the Arts and Manufactures.

By DR. FRANZ LAFAR.

Prof. of Fermentation-Physiology and Bacteriology in the Technical High School, Vienna.

TRANSLATED BY CHARLES T. C. SALTER.

Vol. I.—SCHIZOMYCETIC FERMENTATION. 15s. net.

Vol. II.—EUMYCETIC FERMENTATION. 24s. net.

NOTE.—Part I. of Vol. II. was issued separately at 7s. 6d. Copies of Part II., Vol. II. have, therefore, been bound up to enable those possessing Part I. to complete their copies. The price of Vol. II., Part II., is 18s. net.

"The first work of the kind which can lay claim to completeness in the treatment of a fascinating subject. The plan is admirable, the classification simple, the style is good, and the tendency of the whole volume is to convey sure information to the reader"—*Lancet*.

Crown 8vo, Handsome Cloth. With Diagrams. 7s. 6d. net.

[Companion Volume to "FERMENTS," by the same Author.]

TOXINES AND ANTITOXINES.

By CARL OPPENHEIMER, Ph.D., M.D.,

Of the Physiological Institute at Erlangen.

TRANSLATED FROM THE GERMAN BY

C. AINSWORTH MITCHELL, B.A., F.I.C., F.C.S.

With Notes, and Additions by the Author, since the publication of the German Edition.

"For wealth of detail, we have no small work on Toxines which equals the one under review"—*Medical Times*

In Crown 8vo, Handsome Cloth. Price 7s. 6d. net.

FERMENTS: AND THEIR ACTIONS.

A Text-book on the Chemistry and Physics of Fermentative Changes.

By CARL OPPENHEIMER, Ph.D., M.D.

TRANSLATED BY C. AINSWORTH MITCHELL, B.A., F.I.C., F.C.S.

"Such a veritable *milium in parvo* has never yet appeared."—*Brewers' Journal*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

In Medium 8vo. Fully Illustrated.

A TREATISE ON
CHEMICAL ANALYSIS,
WITH SPECIAL REFERENCE TO THE SILICATE INDUSTRIES.

By J. W. MELLOR, Sc.D.

In Medium 8vo. Handsome Cloth. Illustrated.

CELLULOID.

ITS MANUFACTURE, APPLICATIONS, AND SUBSTITUTES.

Translated from the French of MASSELO, ROBERTS, and CILLARD.

By H. H. HODGSON, M.A.(Camb.), B.Sc.(Lond.), Ph.D.(Heidelberg).

In Crown 8vo. Fully Illustrated. 4s. 6d. net.

WATER ANALYSIS,
FOR SANITARY AND TECHNICAL PURPOSES.

By HERBERT B. STOCKS, F.I.C., F.C.S.

CONTENTS.—Physical Examination, including Colour, Odour, Taste, &c.
—Sanitary Analysis, including Estimation of Total Solids, Free and
Albuminoid Ammonia, Organic Carbon and Nitrogen, Nitrogen as Nitrates
and Nitrites, Chlorine, Oxygen Absorbed, Hardness, &c —Mineral Ana-
lysis, Estimation of Bases and Acids and Calculation of Results.—Gases
Dissolved in Water.—APPENDIX.—TABLES.—INDEX.

In Medium 8vo. Handsome Cloth. Profusely Illustrated. 15s. net.

Modern Destructor Practice.

By W. FRANCIS GOODRICH, Assoc.Inst.C.E., F.I.San.Engrs., &c.

(See page 18.)

SECOND EDITION, Revised. In Medium 8vo, Cloth. Illustrated.
12s. 6d. net.

PAPER TECHNOLOGY:
AN ELEMENTARY MANUAL ON THE MANUFACTURE, PHYSICAL QUALITIES,
AND CHEMICAL CONSTITUENTS OF PAPER AND OF
PAPERMAKING FIBRES.

With Selected Tables for Stationers, Publishers, and Others.

By R. W. SINDALL, F.C.S.

"Exceedingly instructive and particularly useful."—*Paper Makers' Monthly Journal.*

LONDON: CHARLES GRIFFIN & CO, LIM TEO, EXETER STREET, STRAND.

In Crown 8vo. Handsome Cloth. Fully Illustrated. 6s. net.

PEAT: Its Use and Manufacture.

By PHILIP R. BJÖRLING AND FREDERICK T. GISSING.

GENERAL CONTENTS.—Introduction.—The Formation of Peat—Areas and Depth of Bogs in Principal Countries—Manufacture of Peat Fuel, &c.—Cut Peat, Dredged Peat, and Manufactured Peat.—Machinery employed in the Manufacture of Peat Fuel.—Peat Moss Litter, and the Machinery employed in its Manufacture—Peat Charcoal and its Manufacture—Cost of making Peat Fuel and Charcoal.—Other Productions derived from Peat, such as Tar, Manure, Candles, Dyes, Paper, &c.—BIBLIOGRAPHY.—INDEX.

"The treatment throughout is clear and interesting . . . excellent plates."—*Engineering*.

Companion Volume to the above. In Crown 8vo. Cloth. Fully Illustrated. 6s. net.

COMMERCIAL PEAT:

Its Uses and Its Possibilities.

By F. T. GISSING.

"A useful and instructive epitome of the development of the industry."—*Mechanical Engineer*.

In Crown 8vo. Pp. i-xi+451. Price 7s. 6d. net.

British Clays, Shales & Sands.

By A. B. SEARLE, CANTOR LECTURER ON BRICKMAKING.

SECOND EDITION, Thoroughly Revised. In Crown 8vo. Handsome Cloth. 6s. net.

THE CLAYWORKER'S HANDBOOK.

A Manual for all engaged in the Manufacture of Articles from Clay.

By ALFRED B. SEARLE, Cantor Lecturer on Brickmaking.

GENERAL CONTENTS.—Materials used in Clayworking: Clays, Engobes, Glazes, Colours, Water, Fuel, Oils, and Lubricants.—The Preparation of the Clay, Mining and Quarrying; Weathering, Washing, Grinding, Tempering, and Pugging.—Machinery: Rollers, Engines, General Machinery, Sieves, Mixing Machinery, Presses, &c.—Dryers and Drying—Engobing and Glazing.—Setting or Chargin, Transport.—Kilns.—Firing.—Discharging, Sorting, and Packing.—Defects and Waste.—Tests, Analysis and Control.—BRICKMAKING.—INDEX.

"We can thoroughly recommend this handy little book to all our readers."—*Brick and Pottery Trades Journal*.

In Imperial 8vo. Strongly and Elegantly Bound in Half Leather.

Enclosed in Case. Pp. i-xviii + 660. £2 2s. net.

CERAMIC LITERATURE.

Compiled, Classified, and Described by M. L. SOLON,

President of the English Ceramic Society.

An Analytical Index to the Works Published in all Languages on the History and the Technology of the Ceramic Art; also to the Catalogues of Public Museums, Private Collections, and of Auction Sales in which the Description of Ceramic Objects occupy an important place; and to the most important Price Lists of the Ancient and Modern Manufactories of Pottery and Porcelain.

"A work of inestimable value to all serious study of Ceramics."—*Burlington Magazine*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND

In Medium 8vo. Cloth. Pp. i-xiii + 356. With Tables, Illustrations & in the Text, and 36 Plates. 21s. net.

MODERN METHODS OF SEWAGE PURIFICATION.

By G. BERTRAM KERSHAW,

Engineer to the Royal Commission on Sewage Disposal.

CONTENTS.—Introduction.—Historical.—Conservancy Methods and Purification of Sewage.—Drainage Area and Water Supply.—Sewerage Systems.—Rainfall and Storm Water.—Variations in Flow of Sewage.—Composition and Classification of Sewages.—Considerations to be Observed in Selecting the Site for Disposal Works.—Preliminary Processes.—Sludge Disposal.—Land Treatment.—Contact Beds.—Percolating Filters.—Treatment of Trade Refuse.—Effluents and Standards.—Appendix.—INDEX.

"A large and comprehensive work . . . replete with information."—*Journal Royal Sanitary Institute.*

In Large 8vo. Cloth. With 147 Illustrations. 15s. net.

A MANUAL OF

THE PRINCIPLES OF SEWAGE TREATMENT.

By PROF. DUNBAR,

Director of the Institute of State Hygiene, Hamburg.

ENGLISH EDITION BY HARRY T. CALVERT, M.Sc., Ph.D., F.I.C.,
Chief Chemical Assistant, West Riding of Yorkshire Rivers Board.

"We heartily commend the book as a peculiarly fair and impartial statement of the present position of the sewage problem."—*Lancet.*

Beautifully Illustrated, with Numerous Plates, Diagrams, and Figures in the Text. 21s. net.

TRADES' WASTE :

ITS TREATMENT AND UTILISATION.

Handbook for Borough Engineers, Surveyors, Architects, and Analysts.

By W. NAYLOR, F.O.S., A.M. INST. C.E.,

Chief Inspector of Rivers, Ribble Joint Committee.

"There is probably no person in England to-day better fitted to deal rationally with such a subject."—*British Sanitarian.*

SECOND EDITION. In Medium 8vo. Thoroughly Revised and Re-Written.
15s. net.

CALCAREOUS CEMENTS :

THEIR NATURE, PREPARATION, AND USES.

With some Remarks upon Cement Testing.

By GILBERT R. REDGRAVE, Assoc. Inst. C.E.,

Assistant Secretary for Technology, Board of Education, South Kensington,

AND CHARLES SPACKMAN, F.C.S.

"We can thoroughly recommend it as a first-class investment."—*Practical Engineer.*

In Handsome Cloth. 5s. net.

A HANDBOOK FOR CEMENT WORKS' CHEMISTS.

By FRANK B. GATEHOUSE, F.C.S.

GENERAL CONTENTS.—Introduction.—Chemicals and Apparatus.—Books.—Analysis and Calculations of Raw Materials.—Analysis of Fuel, Kiln Gases, Lubricants and Water.—Cement Analysis.—Gypsum, Plaster, &c., Burnt Lime.—APPENDICES.—INDEX.
"Concise . . . excellent . . . a useful addition to Cement Literature."—*Concrete.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

- In Large Crown 8vo. Fully Illustrated. In Two Volumes.
VOLUME I. FOURTH EDITION. Price 7s. 6d. net.
 .. II. THIRD EDITION. READY SHORTLY.

THE CHEMISTRY OF
GAS MANUFACTURE:

A Hand-Book on the Production, Purification, and Testing of Illuminating Gas, and the Assay of the Bye-Products of Gas Manufacture.

By **W. J. ATKINSON BUTTERFIELD, M.A., F.I.C., F.C.S.,**
 Formerly Head Chemist, Gas Works, Beckton, London. E.

"The BEST WORK of its kind which we have ever had the pleasure of reviewing."—*Journal of Gas Lighting.*

In Large Crown 8vo. Handsome Cloth. Illustrated. 6s. net.

THE CALORIFIC POWER OF GAS.

By **J. H. COSTÉ, F.I.C., F.C.S.**

CONTENTS.—Historical.—Calorific Standards.—Constituents of Coal Gas and Similar Gaseous Mixtures.—Their Thermal Properties.—Calorimetry.—Appendix.—INDEX.

SECOND EDITION, Rewritten. Illustrated. 8s. 6d. net.

ACETYLENE:

THE PRINCIPLES OF ITS GENERATION AND USE.

By **F. H. LEEDS, F.I.C., F.C.S.,**

AND **W. J. ATKINSON BUTTERFIELD, M.A., F.I.C., F.C.S.,**
 Consulting Chemist, Author of "The Chemistry of Gas Manufacture."

"We can thoroughly recommend the book to the manufacturer as a reliable work of reference, to the user as supplying valuable hints on apparatus and methods of procedure, and to the student as a safe and certain guide."—*Acetylene.*

Large 8vo. Handsome Cloth. Price 16s. net.

FIRE AND EXPLOSION RISKS:

A Handbook of the Detection, Investigation, and Prevention of Fires and Explosions.

By **DR. VON SCHWARTZ.**

Translated from the Revised German Edition by **C. T. C. SALTER.**

ABBREVED GENERAL CONTENTS.—Fires and Explosions of a General Character—Dangers arising from Sources of Light and Heat.—Dangerous Gases.—Risks Attending Special Industries.—Materials Employed.—Agricultural Products.—Fats, Oils, and Resins.—Mineral Oils and Tar.—Alcohol, &c.—Metals, Oxides, Acids, &c.—Lightning, Ignition Appliances, Fireworks.

"The work affords a wealth of information on the chemistry of fire and kindred topics."—*Fire and Water.*

In handsome Cloth. With 59 Illustrations. 6s. net.

SMOKE ABATEMENT.

A Manual for the Use of Manufacturers, Inspectors, Medical Officers of Health, Engineers, and Others.

By **WILLIAM NICHOLSON,**
 Chief Smoke Inspector to the Sheffield Corporation.

"We welcome such an adequate statement on an important subject."—*British Medical Journal.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SIXTEENTH EDITION, Thoroughly Revised. Price 6s.

PRACTICAL SANITATION: A HAND-BOOK FOR SANITARY INSPECTORS AND OTHERS INTERESTED IN SANITATION.

By GEORGE REID, M.D., D.P.H.,
*Fellow, Mem. Council, and Examiner, Sanitary Institute of Great Britain,
and Medical Officer to the Staffordshire County Council.*

With an Appendix on Sanitary Law.

By HERBERT MANLEY, M.A., M.B., D.P.H.,
Barrister-at-Law.

GENERAL CONTENTS.—Introduction.—Water Supply: Drinking Water, Pollution of Water.—Ventilation and Warming.—Principles of Sewage Removal.—Details of Drainage: Refuse Removal and Disposal.—Sanitary and Insanitary Work and Appliances.—Details of Plumbers' Work.—House Construction.—Infection and Disinfection.—Food, Inspection of; Characteristics of Good Meat; Meat, Milk, Fish, &c., unfit for Human Food.—Appendix: Sanitary Law: Model Bye-Laws, &c.

"A VERY USEFUL HANDBOOK, with a very useful Appendix. We recommend it not only to SANITARY INSPECTORS, but to HOUSEHOLDERS and ALL interested in Sanitary Matters."—*Sanitary Record.*

In Handsome Cloth. With 53 Illustrations. 3s. 6d. net.

LESSONS ON SANITATION.

By JOHN WM. HARRISON, M.R.SAN.I.,

Mem. hon. Assoc. Mun. and County Engineers; Surveyor, Wombwell, Yorks.

"Accurate, reliable, and compiled with conciseness and care."—*Sanitary Record.*

SECOND EDITION, Revised. In Crown 8vo. Handsome Cloth. Profuse
Illustrated. 8s. 6d. net.

SANITARY ENGINEERING:

*A Practical Manual of Town Drainage and Sewage and Refuse Disposal,
For Sanitary Authorities, Engineers, Inspectors, Architects,
Contractors, and Students.*

By FRANCIS WOOD, A.M. INST. C.E., F.G.S.,

Borough Engineer and Surveyor, Fulham; late Borough Engineer, Bacup, Lancs.

GENERAL CONTENTS.

Introduction.—Hydraulics.—Velocity of Water in Pipes.—Earth Pressures and Retaining Walls.—Powers.—House Drainage.—Land Drainage.—Sewers.—Separate System.—Sewage Pumping.—Sewer Ventilation.—Drainage Areas.—Sewers, Manholes, &c.—Trade Refuse.—Sewage Disposal Works.—Bacterial Treatment.—Sludge Disposal.—Construction and Cleansing of Sewers.—Refuse Disposal.—Chimneys and Foundations.

"The volume bristles with information which will be greedily read by those in need of assistance. The book is one that ought to be on the bookshelves of EVERY PRACTICAL ENGINEER."—*Sanitary Journal.*
"A VERITABLE POCKET COMPENDIUM of Sanitary Engineering." "A work which may, in many respects, be considered as COMPLETE . . . COMENDABLY CAUTIOUS . . . INTERESTING . . . SUGGESTIVE."—*Public Health Engineer.*

With Four Folding Plates and Numerous Illustrations. Large 8vo.
8s. 6d. net.

WATER SUPPLY:

A Practical Treatise on the Selection of Sources and the Distribution of Water.

By REGINALD F. MIDDLETON, M. INST. C.E., M. INST. MECH. E., F.S.I.

"As a companion for the student, and a constant reference for the technical man, we anticipate it will take an important position on the bookshelf."—*Practical Engineer.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION. *In Large 8vo. Handsome Cloth. Beautifully Illustrated. With Plates and Figures in the Text. 21s. net.*

ROAD MAKING AND MAINTENANCE:

A Practical Treatise for Engineers, Surveyors, and Others.

WITH AN HISTORICAL SKETCH OF ANCIENT AND MODERN PRACTICE.

By THOS. AITKEN, ASSOC. M. INST. C. E.,

Member of the Association of Municipal and County Engineers; Member of the Sanitary Inst.; Surveyor to the County Council of Fife. Cupar Division.

WITH NUMEROUS PLATES, DIAGRAMS, AND ILLUSTRATIONS.

CONTENTS.—Historical Sketch.—Resistance of Traction.—Laying out New Roads.—Earthworks, Drainage, and Retaining Walls.—Road Materials, of Metal.—Quarrying.—Stone Breaking and Haulage.—Road-Rolling and Bearerfying.—The Construction of New, and the Maintenance of existing Roads.—Carriage Ways and Foot Ways.

"The Literary style is EXCELLENT. . . . A COMPREHENSIVE and EXCELLENT Modern Book, an UP-TO-DATE work. . . . Should be on the reference shelf of every Municipal and County Engineer or Surveyor in the United Kingdom, and of every Colonial Engineer."—*The Surveyor*.

In Handsome Cloth. Fully Illustrated. 10s. 6d. net.

DUSTLESS ROADS. TAR MACADAM.

By J. WALKER SMITH,

City Engineer, Edinburgh.

CONTENTS.—Necessity for Improved and Standard Road Construction.—Tar.—Standardisation of Material.—Aggregate for Macadam.—Different Modes of Preparing and Laying.—Mechanical Mixing.—Effects of Wear, Density, Porosity, Weight.—Scavenging; Watering and Maintenance.—Camber; Gradient, Noiselessness, Hygienic Advantages.—Rolling.—Tractive Effort.—Statistics.—Tar Spraying on Ordinary Macadam Surfaces.—APPENDICES.—INDEX.

"The book is in every respect up-to-date and very suggestive. It is practical in the best sense of the term."—*County and Municipal Record*.

A MANUAL OF CIVIL ENGINEERING PRACTICE.

By F. NOEL TAYLOR, CIVIL ENGINEER. [See p. 18.]

ALSO

THE MAIN DRAINAGE OF TOWNS.

By THE SAME AUTHOR. [See p. 18.]

In Demy 8vo. Handsome Cloth. With Many Tables. 6s. net.

THE THEORY AND PRACTICE OF

ENAMELLING ON IRON AND STEEL.

By JULIUS GRÜNWARD,

Technical Chemist and Works' Manager.

CONTENTS.—Introduction.—The Raw Materials.—The Mixing, Dissolving, and Application of Enamel.—Heating and Pickling Goods in the Bough.—Correct laying on.—Baking Enamelled Ware.—Decoration of Enamelled Objects.—Photo-Ceramics in their Application to Enamels.—General and Statistical Chapter.—The History of Enamels and their Uses.—INDEX.

"Combines the theory and practice of enamelling in a most effective manner."—*Iron and Steel Trades Journal*.

In Large 8vo. Handsome Cloth. With Plates and Illustrations, 7s. 6d. net.

THE MANUFACTURE OF INK.

Handbook of the Production and Properties of Printing, Writing, and Copying Inks

By C. A. MITCHELL, B.A., F.I.C., F.C.S., & T. C. HEPWORTH

"Thoroughly well arranged . . . and of a genuinely practical order."—*British Printer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Large 8vo. Handsome Cloth. Profusely Illustrated. 30s. net.

A TREATISE ON
COLOUR MANUFACTURE.

A Guide to the Preparation, Examination, and Application of all the
Pigment Colours in Practical Use.

BY GEORGE ZERR AND DR. R. RÜBENCAMP.

AUTHORISED ENGLISH TRANSLATION BY DR. C. MAYER, OF BURGDORF.

"This comprehensive guide . . . useful and interesting."—*Oil and Colour Trades Journal*.

In Medium 8vo. Handsome Cloth. Pp. i-xii + 230. Price 10s. 6d. net.

TESTS FOR COAL-TAR COLOURS IN ANILINE LAKES.

BY GEORGE ZERR.

TRANSLATED BY DR. C. MAYER OF BURGDORF.

ABSTRACT OF CONTENTS.—Introductory.—Reactions of Aniline Lakes.—Classification of the Coal-Tar Colour Lakes according to Solubility.—INDEX.

"Of the highest scientific accuracy . . . leaves nothing to be desired in clearness."—*Decorator*.

FIFTH EDITION, Revised and Enlarged. With Illustrations.

PAINTERS' COLOURS, OILS, AND VARNISHES:
A PRACTICAL MANUAL.

BY GEORGE H. HURST, F.C.S.

GENERAL CONTENTS.—Introductory—THE COMPOSITION, MANUFACTURE, ASSAY, and ANALYSIS of PIGMENTS, White, Red, Yellow and Orange, Green, Blue, Brown, and Black—LAKES—Colour and Paint Machinery—Paint Vehicles (Oils, Turpentine, &c., &c.)—Driers—VARNISHES.

"A THOROUGHLY PRACTICAL book . . . Satisfactorily treats of the manufacture of oils, colours, and pigments."—*Chemical Trades' Journal*

In Crown 8vo. Handsome Cloth. With Illustrations. 5s.

THE PAINTER'S LABORATORY GUIDE.

A Student's Handbook of Paints, Colours, and Varnishes.

BY GEORGE H. HURST, F.C.S.

"This excellent handbook, . . . the model of what a handbook should be."—*Oils Colours, and Decoratives*.

THIRD EDITION, Revised. In Crown 8vo. extra. With Numerous Illustrations and Plates (some in Colours), including Original Designs 12s. 6d.

Painting and Decorating:

*A Complete Practical Manual for House
Painters and Decorators.*

BY WALTER JOHN PEARCE,

LECTURER AT THE MANCHESTER TECHNICAL SCHOOL FOR BOOK-PAINTING AND DECORATING.

"A THOROUGHLY USEFUL BOOK . . . GOOD, SOUND, PRACTICAL INFORMATION IN A CLEAR AND CONCISE FORM."—*Plumber and Decorator*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

- THIRD EDITION. In Large 8vo. Handsome Cloth. With 4 Plates and Several Illustrations. 16s. net.

THE CHEMISTRY OF INDIA RUBBER.

Treatise on the Nature of India Rubber, its Chemical and Physical Examination, and the Determination and Valuation of India Rubber Substitutes.

Including the Outlines of a Theory on Vulcanisation.

By CARL OTTO WEBER, PH.D.

"Replete with scientific and also with technical interest. . . . The section on physical properties is a complete *résumé* of every thing known on the subject."—*India-rubber Journal*.

In Handsome Cloth. Fully Illustrated. 10s. 6d. net.

THE MANUFACTURE OF RUBBER GOODS.

By ADOLF HEIL AND DR. W. ESCH.

TRANSLATED BY EDWARD W. LEWIS, A.C.G.I., F.C.S.,
Chemist to Messrs. J. G. INGRAM & SON, London.

GENERAL CONTENTS.—Raw Material and its Preparation.—Vulcanisation.—Rubber Mixings.—Manufacture of Soft Rubber Goods.—Manufacture of Hard Rubber Goods.—Regeneration of Waste Rubber.—Specific Gravity of Rubber Goods.—INDEX.
"Can be recommended as a very practical and useful work."—*Nature*.

In Large Crown 8vo. Fully Illustrated. 5s. net.

GLUE, GELATINE, AND THEIR ALLIED PRODUCTS,

A Practical Handbook for the Manufacturer, Agriculturist, and Student of Technology.

By THOMAS LAMBERT,

Analytical and Technical Chemist.

CONTENTS.—Historical.—GLUE.—GELATINE.—Size and Isinglass.—Treatment of Effluents produced in Glue and Gelatine Making.—Liquid and other Glues, Cements, &c.—Uses of Glue and Gelatine.—Residual Products.—Analysis of Raw and Finished Products.—APPENDIX.—INDEX.

"A sufficient account of modern methods of working, chiefly from a practical standpoint. A book . . . of real value."—*Chemical News*.

In Large 8vo. Handsome Cloth. Fully Illustrated. 15s. net.

LEATHER TRADES' CHEMISTRY.

A Practical Manual on the Analysis of Materials and Finished Products.

By S. R. TROTMAN, M.A., F.I.C.,

Public Analyst for the City of Nottingham, Member of the International Association of Leather Trades' Chemists.

SYNOPSIS OF CONTENTS.—Standard Solutions.—Acids, Alkalies, &c.—Water.—Depilation and Deliming.—Fleshings, &c.—Glue.—Spent Liquors.—Mineral and Vegetable Tanning Agents.—Oils.—Soaps.—Varnishes.—Skin.—Leather.—Dyestuffs.—Degreasing Agents.—Effluents.—GLOSSARY.—INDEX.

"Mr. Trotman has admirably succeeded in his aim. . . . Practically every section of the leather trade chemistry is gone into."—*Leather Trades' Review*.

In Crown 8vo. Handsome Cloth. Pp. i-vi + 114. 3s. 6d. net.

THE CHEMISTRY OF THE COLLOIDS.

TRANSLATED FROM THE GERMAN OF DR. VICTOR PÖSCHL

By DR. H. H. HODGSON.

"An excellent little summary of the subject."—*Chemical News*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

THE TEXTILE INDUSTRIES.

SECOND EDITION, Thoroughly Revised Throughout. In Two Large Volumes. Handsome Cloth. 45s.

A MANUAL OF DYEING:
FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS, STUDENTS,
AND ALL INTERESTED IN THE ART OF DYEING.

BY
E. KNECHT, Ph.D., F.I.C., Head of the Chemistry and Dyeing Department of the Technical School, Manchester; Editor of "The Journal of the Society of Dyers and Colourists;"
CHR. RAWSON, F.I.C., F.C.S., Late Head of the Chemistry and Dyeing Department of the Technical College, Bradford; Member Council of the Society of Dyers and Colourists;

AND **RICHARD LOEWENTHAL, Ph.D.**

GENERAL CONTENTS.—Chemical Technology of the Textile Fabrics—Water—Washing and Bleaching—Acids, Alkalies, Mordants—Natural Colouring Matters—Artificial Organic Colouring Matters—Mineral Colours—Machinery used in Dyeing—Tinctorial Properties of Colouring matters—Analysis and Valuation of Materials used in Dyeing, &c., &c.

"This authoritative and exhaustive work . . . the most complete we have yet seen on the subject."—*Textile Manufacturer.*

In Large 8vo, Handsome Cloth. Pp. i-zv + 405. 16s. net.

THE SYNTHETIC DYE STUFFS,

AND

THE INTERMEDIATE PRODUCTS FROM WHICH THEY ARE DERIVED.

By **JOHN CANNELL CAIN, D.Sc. (MANCHESTER AND TUBINGEN),**
Technical Chemist,

AND **JOCELYN FIELD THORPE, Ph.D. (HEIDELBERG), F.R.S.,**
Lecturer on Colouring Matters in the Victoria University of Manchester.

Part I. Theoretical. Part II. Practical. Part III. Analytical.

"We have no hesitation in describing this treatise as one of the most valuable books that has appeared. . . . Will give an impetus to the study of Organic Chemistry generally."—*Chemical Trade Journal.*

Companion Volume to Knecht & Rawson's "Dyeing." In Large 8vo.
Handsome Cloth, Library Style. 16s. net.

A DICTIONARY OF

DYES, MORDANTS, & OTHER COMPOUNDS
USED IN DYEING AND CALICO PRINTING.

With Formulas, Properties, and Applications of the various substances described and concise directions for their Commercial Valuation, and for the Detection of Adulterants.

By **CHRISTOPHER RAWSON, F.I.C., F.C.S.,**
Consulting Chemist to the Behar Indigo Planters' Association; Co-Author of "A Manual of Dyeing;"

WALTER M. GARDNER, F.C.S.,

Head of the Department of Chemistry and Dyeing, Bradford Municipal Technical College;
Editor of the "Journ. Soc. Dyers and Colourists;"

AND **W. F. LAYCOCK, Ph.D., F.C.S.,**

Analytical and Consulting Chemist.

"Turn to the book as one may on any subject, or any substance in connection with the trade, and a reference is sure to be found. The authors have apparently left nothing out."—*Textile Mercury.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Crown 8vo. Cloth. With Numerous Illustrations. 6s. net.

THE COTTON WEAVERS' HANDBOOK.

A Practical Guide to the Construction and Coating of Cotton Fabrics, with Studies in Design.

By HENRY B. HEYLIN,

Of the Royal Technical Institute, Salford.

"Mr. Heylin's text-book is a very reliable one. It is difficult to mark out any special points among so much excellent matter."—*Dyer and Calico Printer*.

Large 8vo. Profusely Illustrated with Plates and Figures in the Text. 16s. net.

THE SPINNING AND TWISTING OF LONG VEGETABLE FIBRES

(FLAX, HEMP, JUTE, TOW, & RAMIE).

A Practical Manual of the most Modern Methods as applied to the Hacking, Carding, Preparing, Spinning, and Twisting of the Long Vegetable Fibres of Commerce.

By HERBERT R. CARTER, Belfast and Lille.

"Meets the requirements of the Mill Manager or Advanced Student in a manner perhaps more than satisfactory. . . . We must highly commend the work as representing up-to-date practice."—*Nature*.

In Medium 8vo. Handsome Cloth. With about 750 Pages.

The PRINCIPLES & PRACTICE of TEXTILE PRINTING

By E. KNECHT, PH.D., AND J. B. FOTHERGILL.

CONTENTS.—Part I. Introduction.—Part II. Methods of Printing.—Part III. Preparation of Cloth for Printing.—Part IV. Preparation of Printing Colours.—Part V. Treatment of Goods after Printing.—Part VI. Mordants.—Part VII. Styles of Printing: (a) Direct; (b) Dyed; (c) Insoluble Azo-Colour; (d) Discharge; (e) Resist or Reserve; (f) Raised; (g) Printing of Linings; (h) Metal Printing; (i) Crepon or "Crimp."—Part VIII. Finishing of Printed Calicoes.—Part IX. Wool and Half Wool Printing. Part X. Silk and Half Silk Printing.—INDEX.

In Medium 8vo. Handsome Cloth. Fully Illustrated. 16s. net.

THE BLEACHING AND FINISHING OF COTTON.

By S. R. TROTMAN, M.A., F.I.C., AND E. L. THORP, M.I.MECH. E.

CONTENTS.—Structure of Cotton Fibre.—Constituents of Cotton Fibre.—Cotton Testing.—Carbohydrates.—Water.—Bacteria in Bleaching.—Cotton Piece Goods.—Steeping.—Transmission of Cloth.—Alkali Boiling.—Soap.—Soap Making.—Organic Solvents.—Kerls.—Washing Machines.—Bleaching and Bleaching Powder.—Bleaching and Souring Apparatus.—Sodium Hypochlorite and Electrolytic Bleaching Solutions.—Other Bleaching Agents.—Souring Acids and Souring Apparatus.—Processes.—Coloured Goods.—Stains and Discolourations.—Finishing and Materials Used.—Mangling, Drying, and Conditioning.—Stiffening and Maucies.—Auxiliary Machines and Processes.—Bleachers.—Beetling.—Calendering.—Finishing Processes.—INDEX.

"Deserves the attention of practical bleachers, and we can recommend it to them with confidence."—*Textile Mercury*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

CHARLES GRIFFIN & CO.'S PUBLICATIONS.

Large 8vo, Handsome Cloth, with Numerous Illustrations. 9s. net.

TEXTILE FIBRES OF COMMERCE.

A HANDBOOK OF

The Occurrence, Distribution, Preparation, and Industrial Uses of the Animal, Vegetable, and Mineral Products used in Spinning and Weaving.

By WILLIAM I. HANNAN,

Lecturer on Botany at the Ashton Municipal Technical School, Lecturer on Cotton Spinning at the Chorley Science and Art School, &c.

USEFUL INFORMATION. . . . ADMIRABLE ILLUSTRATIONS. . . .—*Textile Recorder*.

In Large 8vo, with Illustrations and Printed Patterns. Price 21s.

TEXTILE PRINTING:

A PRACTICAL MANUAL.

Including the Processes Used in the Printing of

COTTON, WOOLLEN, SILK, and HALF-SILK FABRICS.

By C. F. SEYMOUR ROTHWELL, F.C.S.,

Mem. Soc. of Chem. Ind.; late Lecturer at the Munic. Tech. School, Manchester.

"BY FAR THE BEST and MOST PRACTICAL BOOK ON TEXTILE PRINTING which has yet been brought out, and will long remain the standard work on the subject"—*Textile Mercury*.

Large 8vo. Handsome Cloth. 12s. 6d.

BLEACHING & CALICO-PRINTING.

A Short Manual for Students and Practical Men.

By GEORGE DUERR,

Instructor of the Bleaching, Dyeing, and Printing Department at the Acerrington and Bacup Technical Schools; Chemist and Colourist at the Irwell Erist Works.

ASSISTED BY WILLIAM TURNBULL

(of Turnbull & Stockdale, Limited).

With Illustrations and upwards of One Hundred Dyed and Printed Patterns designed specially to show various Stages of the Processes described.

"Mr. DUERR'S WORK will be found MOST USEFUL. . . . The information given is of GREAT VALUE. . . . The Recipes are THOROUGHLY PRACTICAL."—*Textile Manufacturer*.

THIRD EDITION. New Appendix. Cloth. 76 Illustrations. 5s. net.

DYEING AND CLEANING.

By FRANK J. FARRELL, M.Sc., &c.

GENERAL CONTENTS.—Technology of the Textile Fibres.—Dry Dyeing.—Wet Cleaning.—Wet Dyeing.—Dry Dyeing.—Special Methods, Dyeing and Dyeing Skin Rugs, Feathers, and Hats.—Finishing.—APPENDICES.—INDEX.

Timely and valuable . . . well got up in every way."—*Dyer and Calico Printer*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

• THIRD EDITION, Revised, Enlarged, and Re-issued. Price 6s. net.

A SHORT MANUAL OF
INORGANIC CHEMISTRY.

By A. DUPRÉ, Ph.D., F.R.S.,
AND WILSON HAKE, Ph.D., F.I.C., F.C.S.,
Of the Westminster Hospital Medical School

"AN EXAMPLE OF THE ADVANTAGES OF THE SYSTEMATIC TREATMENT of a Science over the fragmentary style so generally followed By A LONG WAY THE BEST of the small Manuals for Students."—*Analyst*.

In Handsome Cloth. With nearly 50 Illustrations. 3s. 6d. net.

THE ELEMENTS OF CHEMICAL ENGINEERING.

By J. GROSSMANN, M.A., Ph.D., F.I.C.

WITH A PREFACE BY

SIR WILLIAM RAMSAY, K.C.B., F.R.S.

CONTENTS.—The Beaker and its Technical Equivalents.—Distilling Flasks, Liebig's Condensers.—Fractionating Tubes and their Technical Equivalents.—The Air-Bath and its Technical Equivalents.—The Blowpipe and Crucible and their Technical Equivalents.—The Steam Boiler and other Sources of Power.—General Remarks on the Application of Heat in Chemical Engineering.—The Funnel and its Technical Equivalents.—The Mortar and its Technical Equivalents.—Measuring Instruments and their Technical Equivalents.—Materials Used in Chemical Engineering and their Mode of Application.—Technical Research and the Designing of Plant.—Conclusion.—Chemicals and Materials.—INDEX.

"Excellent. . . . Every student of chemistry attending a technical course should obtain a copy."—*Chemical News*.

LABORATORY HANDBOOKS BY A. HUMBOLDT SEXTON,

Professor of Metallurgy in the Glasgow and West of Scotland Technical College.

OUTLINES OF QUANTITATIVE ANALYSIS.

FOR THE USE OF STUDENTS.

With Illustrations. FIFTH EDITION. Crown 8vo, Cloth, 2s.

"A COMPACT LABORATORY GUIDE for beginners was wanted, and the want has been WELL SUPPLIED. . . . A good and useful book."—*Lancet*.

OUTLINES OF QUALITATIVE ANALYSIS.

FOR THE USE OF STUDENTS.

With Illustrations. FOURTH EDITION, Revised. Crown 8vo, Cloth, 3s. 6d.

"The work of a thoroughly practical chemist."—*British Medical Journal*.
"Compiled with great care, and will supply a want."—*Journal of Education*.

ELEMENTARY METALLURGY:

Including the Author's Practical Laboratory Course.

[See p. 52.]

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

THIRD EDITION, Revised and Enlarged. Large Crown 8vo, with numerous
Illustrations. 3s. 6d.

THE FLOWERING PLANT,
WITH A SUPPLEMENTARY CHAPTER ON FERNS AND MOSSES,
As Illustrating the First Principles of Botany.

By J. R. AINSWORTH DAVIS, M.A., F.Z.S.,
Prof. of Biology, University College, Aberystwyth; Examiner in Zoology,
University of Aberdeen.

It would be hard to find a Text-book which would better guide the student to an accurate knowledge of modern discoveries in Botany. . . . The SCIENTIFIC ACCURACY of statement, and the concise exposition of FIRST PRINCIPLES make it valuable for educational purposes. In the chapter on the Physiology of Flowers, an *admirable résumé*, drawn from Darwin, Hermann Müller, Kerner, and Lubbock, of what is known of the Fertilization of Flowers, is given "*Journal of Botany*."

POPULAR WORKS ON BOTANY BY MRS. HUGHES-GIBB.

With Illustrations. Crown 8vo. Cloth. 2s. 6d.

HOW PLANTS LIVE AND WORK:

A Simple Introduction to Real Life in the Plant-world, Based on Lessons originally given to Country Children.

By ELEANOR HUGHES-GIBB.

"The attention of all interested in the Scientific Training of the Young is requested to this **DELIGHTFULLY FRESH** and **CHARMING LITTLE BOOK**. It ought to be in the hands of every Mother and Teacher throughout the land."

"The child's attention is first secured, and then, in language **SIMPLE, YET SCIENTIFICALLY ACCURATE**, the first lessons in plant-life are set before it."—*Natural Science*.

"In every way well calculated to make the study of Botany **ATTRACTIVE** to the young."—*Scottman*.

With Illustrations. Crown 8vo. Gilt 2s. 6d.

THE MAKING OF A DAISY;
"WHEAT OUT OF LILIES;"

And other Studies from the Plant World.

A Popular Introduction to Botany.

By ELEANOR HUGHES-GIBB,

Author of *How Plants Live and Work*.

"A **MAJESTIC** little introduction to the study of Flowers."—*Journal of Botany*.
"The book will afford real assistance to those who can derive pleasure from the study of Nature in the open. . . . The literary style is commensurable."—*Knowledge*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

• "Boys COULD NOT HAVE A MORE ALLURING INTRODUCTION to scientific pursuits than these charming-looking volumes."—*Letter to the Publishers from the Head master of one of our great Public Schools.*

SECOND EDITION, Revised. Handsome Cloth. 6s. net.

OPEN-AIR STUDIES IN BOTANY:

SKETCHES OF BRITISH WILD FLOWERS
IN THEIR HOMES.

By R. LLOYD PRAEGER, B.A., M.R.I.A.

Illustrated by Drawings from Nature by S. Rosamond Praeger,
and Photographs by R. Welch.

GENERAL CONTENTS.—A Daisy-Starred Pasture—Under the Hawthorne—By the River—Along the Shingle—A Fragrant Hedgerow—A Condemned Bog—Where the Samphire grows—A Flowery Meadow—Among the Corn—a Study in Weeds)—In the Home of the Alpines—A City Rubbish-Heap—Glossary.

"A FRESH AND STIMULATING book . . . should take a high place . . . The illustrations are drawn with much skill."—*The Times.*

"BEAUTIFULLY ILLUSTRATED. . . . One of the MOST ACCURATE as well as INTERESTING books of the kind we have seen."—*Athenaeum.*

"Redolent with the scent of woodland and meadow."—*The Standard.*

With 12 Full-Page Illustrations from Photographs. Cloth.
Second Edition, Revised. 8s. 6d.

OPEN-AIR STUDIES IN GEOLOGY:

An Introduction to Geology Out-of-doors.

By GRENVILLE A. J. COLE, F.G.S., M.R.I.A.,

Professor of Geology in the Royal College of Science for Ireland,
and Examiner in the University of London.

GENERAL CONTENTS.—The Materials of the Earth—A Mountain Hollow—Down the Valley—Along the Shore—Across the Plains—Dead Volcanoes—A Granite Highland—The Annals of the Earth—The Surrey Hills—The Folds of the Mountains.

"The FASCINATING 'Open-Air Studies' of PROF. COLE give the subject a glow of ANIMATION . . . cannot fail to arouse keen interest in geology."—*Geological Magazine.*

"A CHARMING BOOK, beautifully illustrated" — *Athenaeum.*

Beautifully Illustrated. With a Frontispiece in Colours, and Numerous
Specially Drawn Plates by Charles Whymper. 7s. 6d.

OPEN-AIR STUDIES IN BIRD-LIFE:

SKETCHES OF BRITISH BIRDS IN THEIR HAUNTS.

By CHARLES DIXON.

The Spacious Air.—The Open Fields and Downs.—In the Hedgerows.—On Open Heath and Moor.—On the Mountains.—Amongst the Evergreens.—Copses and Woodland.—By Stream and Pool.—The Sandy Wastes and Mud-flats.—Sea-laved Rocks.—Birds of the Cities.—INDEX.

"Enriched with excellent illustrations. A welcome addition to all libraries."—*Westminster Review.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

AN ELEMENTARY TEXT-BOOK OF PHYSICS.

By R. WALLACE STEWART, D.Sc. (LOND.)

In Four Volumes. Crown 8vo. Cloth. Each Fully Illustrated.
Sold Separately.

VOL. I. Pp. i-vii+414. With 187 Illustrations. 4s. 6d. net.

GENERAL PHYSICS.

CONTENTS.—Introductory.—Scalar and Vector Quantities.—Measurement of Length, Area, and Volume.—Measurement of Time.—Measurement of Mass.—Velocity.—Acceleration.—Circular Motion and Simple Harmonic Motion.—Force.—Work and Energy.—Composition and Resolution of Forces.—Centre of Gravity.—Equilibrium of Forces.—Friction.—The Balance.—General Properties of Matter.—Properties of Solids.—Hydrostatics.—Experimental Determination of Specific Gravity and Density.—Properties of Liquids.—Properties of Liquids (*continued*).—Properties of Gases.—INDEX

VOL. II. Pp. i-vii+141. Profusely Illustrated. 2s. 6d. net.

SOUND.

CONTENTS.—Simple Harmonic Vibration.—Production of Sound.—Wave Motion.—Propagation of Sound.—Characteristics of Sound.—Reflection and Refraction of Sound.—Velocity of Sound in Air and Water.—Transverse Vibration of Strings.—Longitudinal Vibration of Rods and Columns of Air.—INDEX.

"Should supply the much-felt need of an elementary treatment of this subject . . . distinctly good."—*Nature*.

VOL. III. Pp. i-vii+219. With 142 Illustrations. 3s. 6d. net.

LIGHT.

CONTENTS.—Introductory.—Rectilinear Propagation of Light.—Photometry.—Reflection at Plane Surfaces.—Reflection at Spherical Surfaces.—Refraction.—Refraction through Lenses.—Dispersion.—INDEX.

"This elementary treatise resembles Part II. (*continued*) in its attractiveness . . . the treatment is good . . . excellent diagrams . . . very clear."—*Journal of Inst. of Teachers in Technical Institutes*.

VOL. IV. Pp. i-v+242. With 84 Illustrations. 3s. 6d. net.

HEAT.

CONTENTS.—Introductory.—Thermometry.—Expansion of Solids.—Expansion of Liquids.—Expansion of Gases.—Calorimetry.—Specific Heat.—Liquefaction and Solidification.—Vaporisation and Condensation.—Conduction of Heat.—Convection.—Mechanical Equivalent of Heat.—Radiation.—INDEX.

In Large 8vo. With Bibliography, Illustrations in the Text, and Seven Plates. 12s. 6d.

THE MEAN DENSITY OF THE EARTH.

An Essay to which the Adams Prize was Adjudged in 1893 in the University of Cambridge

By J. H. POYNTING, Sc.D., F.R.S.

"Cannot fail to be of great and general interest."—*Athenæum*.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

• DR. STEWART'S ELEMENTARY TEXT-BOOK OF PHYSICS
was designed as an introduction to the following:—

A TEXT-BOOK OF PHYSICS.

By J. H. POYNTING, Sc.D., F.R.S.,
Professor of Physics, Birmingham University,

And Sir J. J. THOMSON, M.A., F.R.S.,
Professor of Experimental Physics in the University of Cambridge.

In Five Volumes. Large 8vo. Sold Separately.

INTRODUCTORY VOLUME. FIFTH EDITION, Revised. Fully Illustrated.
10s. 6d.

PROPERTIES OF MATTER.

CONTENTS.—Gravitation.—The Acceleration of Gravity.—Elasticity.—Stresses and Strains.—Torsion.—Bending of Rods.—Spiral Springs.—Collision.—Compressibility of Liquids.—Pressures and Volumes of Gases.—Thermal Effects Accompanying Strain.—Capillarity.—Surface Tension.—Laplace's Theory of Capillarity.—Diffusion of Liquids.—Diffusion of Gases.—Viscosity of Liquids.—INDEX.

"We regard this book as quite indispensable not merely to teachers but to physicists of every grade above the lowest."—*University Correspondent*.

VOLUME II. FIFTH EDITION. Fully Illustrated. Price 8s. 6d.

SOUND.

CONTENTS.—The Nature of Sound and its chief Characteristics.—The Velocity of Sound in Air and other Media.—Reflection and Refraction of Sound.—Frequency and Pitch of Notes.—Resonance and Forced Oscillations.—Analysis of Vibrations.—The Transverse Vibrations of Stretched Strings or Wires.—Pipes and other Air Cavities.—Rods.—Plates.—Membranes.—Vibrations maintained by Heat.—Sensitive Flames and Jets.—Musical Sound.—The Superposition of Waves.—INDEX.

"The work . . . may be recommended to anyone desirous of possessing an EARLY UP-TO-DATE STANDARD TREATISE ON ACOUSTICS."—*Literature*.

VOLUME III. FOURTH EDITION, Revised. Fully Illustrated. Price 16s.

HEAT.

CONTENTS.—Temperature.—Expansion of Solids—Liquids.—Gases.—Circulation and Convection.—Quantity of Heat; Specific Heat.—Conductivity.—Forms of Energy; Conservation; Mechanical Equivalent of Heat.—The Kinetic Theory.—Change of State; Liquid, Vapour.—Critical Points.—Solids and Liquids.—Atmospheric Conditions.—Radiation.—Theory of Exchanges.—Radiation and Temperature.—Thermodynamics.—Isothermal and Adiabatic Changes.—Thermodynamics of Changes of State, and Solutions.—Thermodynamics of Radiation.—INDEX.

"Well up-to-date, and extremely clear and exact throughout. . . . As clear as it would be possible to make such a text-book."—*Nature*.

Remaining Volumes in Preparation—

LIGHT; MAGNETISM AND ELECTRICITY.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION, Revised. In Crown 8vo. With Diagrams. Cloth.

AN INTRODUCTION TO
THE THEORY OF STATISTICS.

By G. UDNY YULE,

Honorary Secretary of the Royal Statistical Society of London, &c.

CONTENTS.—Introduction. Part I.—The Theory of Attributes.—Notation and Terminology.—Consistence.—Association.—Partial Association.—Manifold Classification. Part II.—The Theory of Variables.—Frequency Distribution.—Averages.—Measures of Dispersion, &c.—Correlation.—Do. Practical Applications and Methods.—Miscellaneous Theorems Involving the use of the Correlation Coefficient.—Partial Correlation. Part III.—Theory of Sampling.—Simple Sampling of Attributes.—Effects of Removing the Limitations of Simple Sampling.—The Binomial Distribution and the Normal Curve.—Normal Correlation.—The Simpler Cases of Sampling for Variables.—Percentiles and Mean.

"Well calculated to hold the attention of the student or teacher of economic subjects."—*Statist.*

Twenty-eighth Annual Issue. Handsome cloth, 7s. 6d.

(To Subscribers, 6s.)

THE OFFICIAL YEAR-BOOK
OF THE
**SCIENTIFIC AND LEARNED SOCIETIES OF GREAT BRITAIN
AND IRELAND.**

COMPILED FROM OFFICIAL SOURCES.

Comprising (together with other Official Information) **LISTS** of the **PAPERS** read during the Session 1910-1911 before all the **LEADING SOCIETIES** throughout the Kingdom engaged in the following **Departments of Research** :—

- | | |
|--|---|
| 1. Science Generally: <i>i.e.</i> , Societies occupying themselves with several Branches of Science, or with Science and Literature jointly. | 5 6. Economic Science and Statistics. |
| 2. Mathematics and Physics. | 5 7. Mechanical Science, Engineering, and Architecture. |
| 3. Chemistry and Photography. | 5 8. Naval and Military Science. |
| 4. Geology, Geography, and Mineralogy. | 5 9. Agriculture and Horticulture. |
| 5. Biology, including Microscopy and Anthropology. | 5 10. Law. |
| | 5 11. Literature. |
| | 5 12. Psychology. |
| | 5 13. Archaeology. |
| | 5 14. MEDICINE. |

"FILLS A VERY REAL WANT."—*Engineering.*

"INDISPENSABLE to any one who may wish to keep himself abreast of the scientific work of the day."—*Edinburgh Medical Journal.*

"It goes almost without saying that a Handbook of this subject will be in time one of the most generally useful works for the library or the desk."—*The Times.*

Copies of the **FIRST ISSUE**, giving an Account of the History Organization, and Conditions of Membership of the various Societies, and forming the groundwork of the Series, may still be had, price 7/6. *Also Copies of the Issues following.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

