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THE THERMAL DISSOCIATION OF CADMIUM CARBONATE.

By P. Y. Narayana and H. E. Watson.

Owing to its comparatively low dissociation temperature, cadmium carbonate is a convenient substance to use for studying the relation between dissociation pressure and temperature, and several papers have been published on the subject.

Centnerszwer and Andrussov (*Z. physikal. Chem.*, 1924, **111**, 79) measured the dissociation pressures by both static and dynamic methods and found that the results could be expressed by the formula

$$\log p = -12 \cdot 44 + 0 \cdot 02439\ T.$$

Measurable dissociation occurred at 265° and atmospheric pressure was reached at 357°. Mazzetti (*Atti R. Accad. Lincei*, 1924, [5], **33, II**, 46) found the latter temperature to be 332 and 355° using two different methods. Andrussov (*Z. physikal. Chem.*, 1925, **115**, 273) as the result of a large number of measurements in which equilibrium was approached from both directions found that the formula

$$\log p = -Q_0/4 \cdot 571\ T + 1 \cdot 75 \log T - eT/4 \cdot 571 + 3 \cdot 2$$

where $Q_0 = 21{,}500$ cals., and $e = 0 \cdot 003435$, gave an accurate representation of the results. Measurements of the velocity of decomposition and recombination were also made and it was shown that the carbonate became more active, *i.e.*, reached the equilibrium position more rapidly when it had been decomposed and regenerated several times. According to this formula the dissociation temperature is 344°. Jander (*Z. anorg. Chem.*, 1928, **168**, 113) confirmed these results by observing the temperatures at which the substance heated in a closed vessel containing carbon dioxide at different pressures remained constant in weight. The range studied was 340—510° and the value found for the dissociation temperature was 345°.

The results detailed above are more discordant than might be expected and it was, therefore, decided to make additional experiments with the object of ascertaining, if possible, the reason for the discrepancy. A series of measurements by the static method in the region 260—360° yielded results which agreed well with a simple logarithmic equation although differing somewhat from those of former observers, the dissociation temperature being 352°. The investigation was then extended to lower temperatures at which the vapour pressure was of the order of 1 mm. and it was observed that reproducible results could not be obtained in successive experiments with the same material, a marked diminution in pressure being noted. The original experiments were then repeated with improved temperature control and the same phenomenon was observed. It thus became clear that the system was not simple, but that the dissociation pressure was a function of the amount of oxide in the solid phase.

EXPERIMENTAL.

The cadmium carbonate used was prepared by mixing hot aqueous solutions of equimolecular proportions of pure cadmium sulphate and potassium carbonate, filtering and washing the precipitate with hot water, until no trace of sulphate could be detected in the filtrate. The precipitate was then dried at 100° but as it still retained 0·8 per cent. of moisture it was heated at about 300° for four hours in a stream of pure dry carbon dioxide. Estimation of carbon dioxide in the dried preparation gave 25·70 per cent. as a mean of three concordant determinations, theory requiring 25·53 per cent.

The apparatus used is shown in Fig. I. For temperatures up to 200° the substance was sealed into the small soft glass bulb A immersed in an electrically heated oil thermostat the temperature of which remained constant to ± 0 2° over long periods of time. Pressures were measured on a rotating manometer of the type described by Reden (*Physikal Z.*, 1909, **10,** 316) which would read up to 2 mm. with an accuracy of 0·01 mm. For higher temperatures, the double walled pyrex tube B similar to the one described by Brüning (*Chem. Fabrik.*, 1932, 17) was used. The annular space was filled with mercury which formed a thermoregulator and controlled the heating current of the

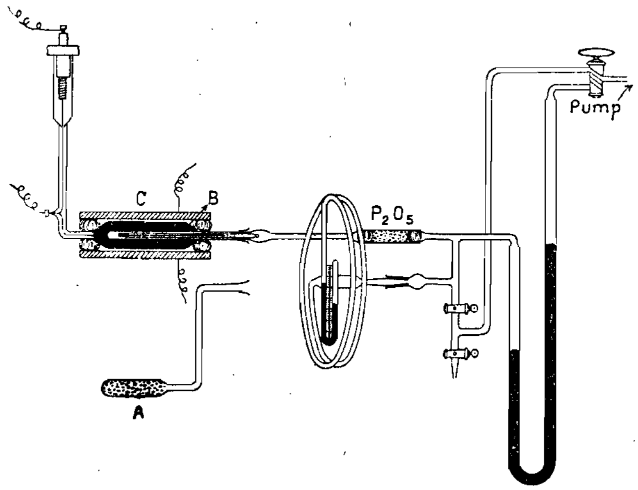

Fig. I.

oven C by means of a relay. The main disadvantage of this arrangement was the distinct lag which occurred between the switching on or off of the current and the corresponding heating or cooling of the tube. This was minimised as far as possible by allowing a steady current to pass, just insufficient to maintain the tube at the required temperature and arranging for the relay to short circuit a resistance when the temperature became too low. The range of temperature was about ± 0·5° at 300° and ± 0·7° at 335°, the temperatures being determined by means of a calibrated mercury thermometer enclosed inside the apparatus.

Before making measurements at higher pressures, the volume of the apparatus and manometer was determined at different pressures by filling it with air which was then pumped off and measured. In this way an estimate could be formed of the amount of gas which had been evolved by the cadmium carbonate at any stage.

RESULTS.

The results obtained at the lower temperatures are shown in Table I.

TABLE I.

	Temperature	Time in days		Equilibrium pressure mm.
(1)	175 ± 0·2°	60	(i)	0·425
		60	(ii)	0·284
(2)	192·5 ± 0·2°	34	(i)	1·75
		44	(ii)	1·35
		38	(iii)	0·71
		40	(iv)	0·135

Before commencing the measurements the bulb containing the carbonate was evacuated and heated. At a temperature below 100° the pressure rose to 20 mm. probably owing to adsorbed gas since a bicarbonate of cadmium has not been recorded. The gas was pumped off, any water vapour being removed by the phosphorus pentoxide, and the pressure fell to a very low value. The temperature was then raised to 175° when a further small evolution of gas took place owing to decomposition of the carbonate itself. Pumping was continued at intervals for two hours. From the quantity of carbon dioxide obtained it was estimated that not more than 1 per cent. of the carbonate was decomposed at this stage. The pump was shut off and the pressure allowed to rise. Attainment of equilibrium was very slow but after 60 days an approximately constant pressure was reached. The gas was then removed and the experiment repeated, when it was found that the rate of decomposition and the final pressure were much less than before. The temperature was next raised to 192·5° and results i–iv obtained in succession, the gas being pumped off when the pressure had become approximately constant. The progress of these experiments is shown in greater detail in Fig. II. The quantity of carbonate decomposed at the end was not determined with certainty but was of the order of two per cent.

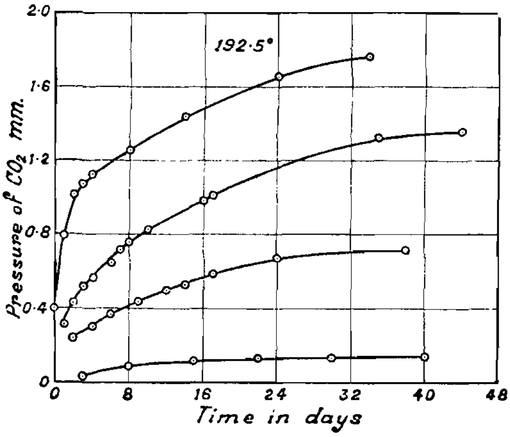

Fig. II.

Before making measurements at the higher temperatures the carbonate was heated at 200° at a low pressure to remove adsorbed gas and moisture, and carbon dioxide admitted into the apparatus until the pressure reached 104 mm. so that the amount of carbonate decomposed on heating would be small. Equilibrium was attained after heating for 3–4 days, the rate of rise in pressure being shown in Figs. III and IV.

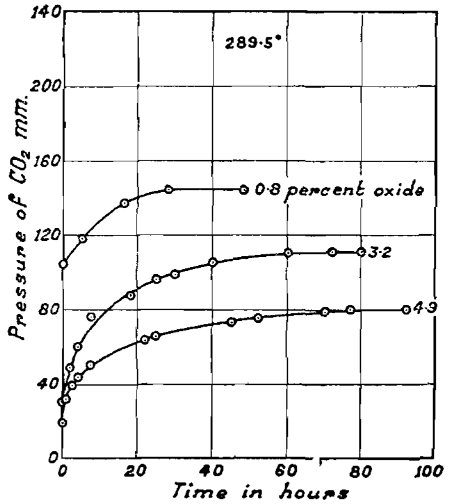

Fig. III.

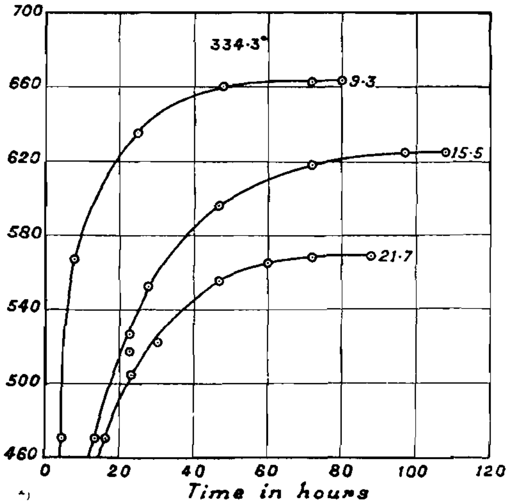

Fig. IV.

The final pressures p and the number of grams g of cadmium oxide in 100 g. of undissociated carbonate at equilibrium are shown in Table II.

TABLE II.

Equilibrium pressures of different mixtures.

T	g	p	$(p_0 - p)/g$
289·5	0·0	(159)	
,,	0·8	144	18·7
,,	3·2	111	15·0
,,	4·9	80	16·1
334·3	0·0	(730)	
,,	9·3	664	7·1
,,	15·5	625	6·8
,,	21·7	577	7·1

If the values of p are plotted against those of g, an approximation to a straight line is obtained in each case so that p_0 the dissociation pressure of the undecomposed carbonate can be obtained by extrapolation. The figures in the last column show the fall in dissociation pressure due to 1 per cent. of oxide and it is remarkable that the change is much greater not only relatively but absolutely, at the lower temperature. Fig. II shows that at still lower temperatures the relative change is very great, about one per cent. of oxide reducing the pressure to 1/14th of its initial value. The exact relation between the relative lowering of pressure produced by a given amount of oxide and the temperature is obscure and cannot be determined without further experimental results. These are somewhat difficult to obtain owing to the long period required for the attainment of equilibrium at the lower temperatures. It is evident, however, that Raoult's law is not obeyed. When the vapour pressure is very low, the results may be complicated by the slow evolution of adsorbed gas from the carbonate and walls of the tube and since the rate of formation of the carbonate is exceedingly small, the observed values may be too high. Too much reliance must not therefore be placed upon the figures of table I.

While the present experiments were in progress Afanasiew and Roginsky in a preliminary communication (*Z. physikal. Chem.*, 1932, **18**, 360), stated that an X-ray examination indicated the existence of solid solutions of the oxide in the carbonate, a phenomenon which is in accordance with the results we have obtained.

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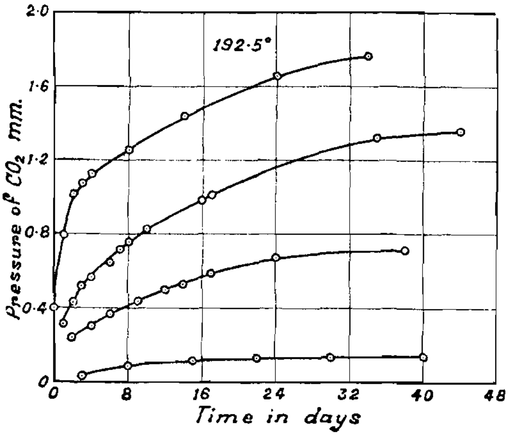

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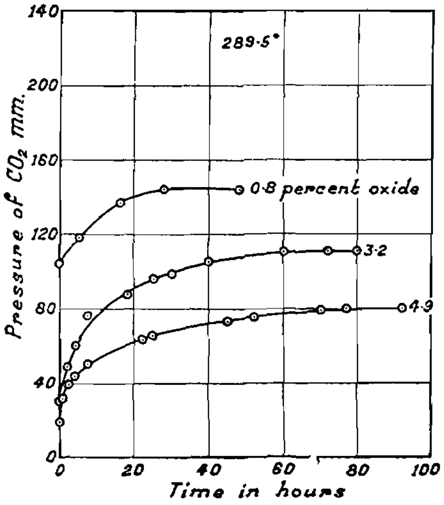
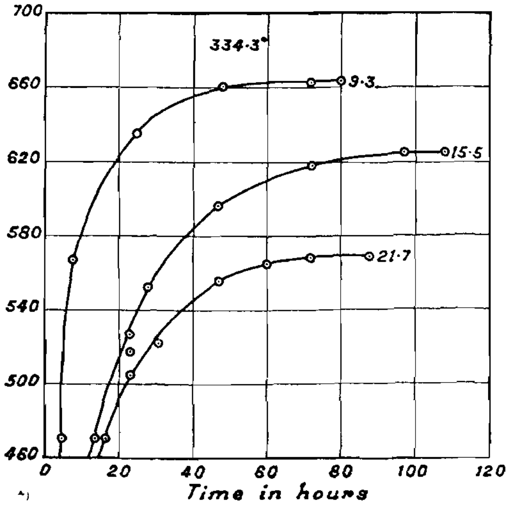


Fig. III.



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SUMMARY.

The dissociation pressure of cadmium carbonate has been measured at various temperatures by a static method and has been found to depend upon the quantity of oxide present.

No simple relation between the lowering of pressure and the amount of oxide has been found, the actual depression for the same proportion of oxide being more at 290° than at 334°. The effect is very marked at lower temperatures.

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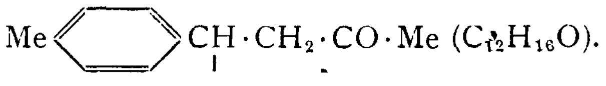
STUDIES IN INDIAN ESSENTIAL OILS.

V. ESSENTIAL OIL FROM THE RHIZOMES OF *CURCUMA LONGA*, LINN.

By N. C. Kelkar and B. Sanjiva Rao.

Curcuma longa is cultivated extensively all over India for the familiar turmeric rhizomes, over 60,000 acres being devoted to this crop. It is an indigenous plant in India and China, and is now naturalised in the Philippines, Java and Formosa. In India, it is chiefly grown in Madras, Bombay and Bengal and has been exported for many years to Great Britain, America, Germany, Persia and Turkey, where it is mainly used for colouring various food-stuffs and as a condiment. Special dyestocks have been produced in India by the careful selection of centuries of cultivation. Turmeric is a direct colour, giving a bright yellow, not removed by water but fading in sunlight. Its present importance is more as a condiment, flavouring material and in medicine.

Although the rhizome itself is an important article of trade, the oil from it is seldom distilled and is not of any commercial importance. It is, however, not without practical interest, as to it turmeric owes its aromatic taste and smell. The oil, extracted from Bengal turmeric, has been often subjected to chemical investigation (Bolley, Suida and Daube, *J. pr. Chem.*, 1868, **103,** 474; Ivanow and Gajewoskey, *Ber.*, 1872, **5,** 1103; Fluckiger, *ibid.*, 1876, **9,** 470; Kachler, *ibid.*, 1870, **3,** 713; Jackson and Menke, *Amer. Chem. J.*, 1882, **4,** 368; 1884, **6,** 81; Jackson and Warren, *ibid.*, 1896, **18,** 111; Schimmel's Report, 1890, 28; Rupe, *Ber.*, 1907, **40,** 4909; Rupe, Luksch and Steinbach, *ibid.*, 1909, **42,** 2515; Rupe and Steinbach, *ibid.*, 1910, **43,** 3465; Rupe and Wiederkehr, *Helv. Chim. Acta*, 1924, **7,** 654), but there is still considerable doubt as to its main constituents, only the presence of *d*-α-phellandrene having been established with certainty. The chief constituent according to Jackson and his collaborators is an alcohol turmerol to which the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$ has been assigned (Parry, *The Chemistry of Essential Oils and Artificial Perfumes*, 4th Edition, 1921, 107). The ketone curcumone discovered by Rupe in 1907 is not an original constituent of the oil but is formed by the action of alkali or acid on its main fraction. It has been recently synthesised by Rupe and Wiederkehr (*loc. cit.*) who have confirmed its structure to be



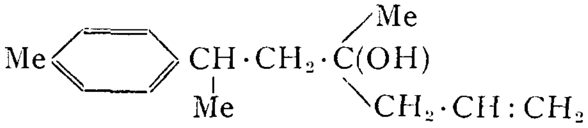
$$\mathrm{Me{-}C_6H_4{-}CH(-)\cdot CH_2\cdot CO\cdot Me}\ (C_{12}H_{16}O).$$

Unlike the oils examined hitherto, which were extracted from the rhizomes with a solvent and then steam-distilling the extract, the oil used in the present investigation was obtained by directly steam-distilling the powdered rhizomes. A detailed examination of the oil has revealed the presence of a number of new constituents. In the lower boiling portions of the oil, besides *d*-α-phellandrene, the presence of *d*-sabinene, cineol and borneol has been confirmed. The sesquiterpenes mainly consist of the monocyclic sesquiterpene zingiberene confirmed by the formation of the dihydrochloride (m.p. 169°), nitrosochloride (m.p. 96°), nitrosate (m.p. 86–87°) and nitrosite (m.p. 96°). Next to oil of ginger which belongs to the same natural order, turmeric oil would appear to be the most suitable source of this sesquiterpene. Its occurrence has been observed so far in only two other oils, Curcuma zedoaria (*Jour. Ind. Inst. Sci.*, 1928, **11A,** 196) and Thymus serpyllum (*ibid.*, 1932, **15A,** 83).

The main bulk of the oil consists of a mixture of sesquiterpene ketones and sesquiterpene alcohols. On treatment with hydroxylamine hydrochloride according to Stillman and Reed (*Perf. and Essent. Oil Rec.*, 1932, **23,** 278) a carbonyl value of 150 (number of milligrams of potassium hydroxide equivalent to hydroxylamine required for one gram of the oil) was obtained indicating 57·5, 58·1 or 58·6 per cent. ketone as $C_{15}H_{20}O$, $C_{15}H_{22}O$ or $C_{15}H_{24}O$ respectively. When the ketones from the turmeric oil were being investigated by the authors a preliminary note appeared by A. Pfau (*Helv. Chim. Acta*, 1932, **15,** 1481) assigning a constitution to the ketones from the oils of turmeric and cedar but no data which led to these structures being assigned have so far been published. It was, therefore, thought desirable to put the results we have obtained on record. In spite of the wide distribution of the terpene ketones, the occurrence of sesquiterpene ketones has been discovered only recently. The first members of this class to be isolated and to have their structure fully elucidated are the Ermephila ketones described lately by Simonsen and his collaborators (*J. C. S.*, 1932, **131,** 2744).

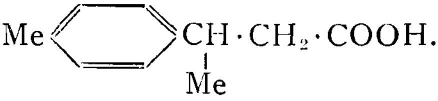
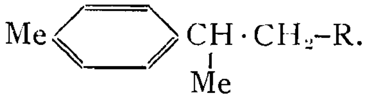
The fraction 158–165°/11 mm. which forms nearly 60 per cent. of the oil was treated with semicarbazide, a liquid semicarbazone being formed, and then steam-distilled. The distillate consisted mainly of tertiary sesquiterpene alcohols ($C_{15}H_{24}O$ or $C_{15}H_{22}O$) and a small quantity of curcumone which was removed by again treating with semicarbazide. The presence of curcumone shows that the sesquiterpene ketones decompose to an appreciable extent on mere boiling with semicarbazide hydrochloride and sodium acetate giving curcumone. The sesquiterpene alcohols freed from the ketones were further purified by benzoylation and distilling the non-alcoholic part. The absence of reaction with phthalic anhydride showed that the alcohols were tertiary. The sesquiterpene alcohols yield curcumone by boiling with alcoholic potash under Rupe's conditions (*loc. cit.*).

Grignard (*Comp. rend.*, 1923, **176**, 1860) found that certain ethylenic tertiary alcohols decompose on distillation into ketones and that a trace of acid or alkali catalyses the reaction. He found (*ibid.*, 1926, **182**, 299) that as the temperature of distillation increased dehydration of the alcohol decreased and the ketonic decomposition increased. Thus allyl-methyl-benzyl carbinol gives 90 per cent. phenylacetone and allyl-methyl-phenyl carbinol 80 per cent. acetophenone. It was thought that curcumone is formed in a similar manner from the sesquiterpene alcohol. A tertiary alcohol $C_{15}H_{22}O$,



was synthesised from curcumone and magnesium-allyl-bromide, but the resulting alcohol, although it formed curcumone on distilling at ordinary pressure, was unaffected by boiling with strong alkali showing that it was not identical with the alcohol occurring in the oil.

Rupe discovered, as already stated, that the fraction 158–165°/11 mm. is converted into a ketone curcumone (semicarbazone m.p. 126°) by boiling with alcoholic potash. This fraction was separated into several portions by efficient fractionation but none gave any derivatives of curcumone showing that it is not an original constituent of the oil. Hintikka prepared (*Ann. Acad. Sci. Fennicae*, 1923, **19A**, 6) from a ten-year old oil by treating with sodium ethylate in alcoholic solution three specimens of curcumone and isolated two more semicarbazones (m.p. 129° and 153–154°) besides the one melting at 126°, showing that ketones other than curcumone may also be formed from turmeric oil. To examine whether ketones other than curcumone are formed by the action of alcoholic potash on the fraction 158–165°/11 mm., the latter was split up into smaller fractions, and the yield and properties of curcumone obtained from several fractions have been recorded, the higher boiling fractions giving better yields of curcumone. The fraction 152–165°/10 mm. gives about 70 per cent. yield of curcumone. The curcumone semicarbazone (m.p. 125–126°) and the benzylidene curcumone (m.p. 106°) prepared from different fractions, were identical showing that the same curcumone is formed. The difference observed by Hintikka is probably due to its being a very old sample of oil and to the changes which curcumone itself undergoes when subjected to chemical treatment.

The oxidation of the sesquiterpene ketones which form the main bulk of the oil, with dilute nitric acid, yielded *p*-toluic and terephthalic acids as observed by Jackson and Menke (*loc. cit.*) and in addition oxalic acid and an infusible acid were also formed. Owing to the small yield and the difficulty of purification, the latter has not been identified. An acid $C_{11}H_{14}O_2$ (m.p. 42·5–43°) was obtained by oxidation of these fractions with potassium permanganate in aqueous or acetone solution. The yield of the acid was doubled in the latter case. This acid was found to be identical with curcumic acid obtained by Rupe and Wiederkehr (*loc. cit.*) by oxidising curcumone with sodium hypobromite and found to have the structure  The acid $C_{11}H_{14}O_2$ (m.p. 33–34°) obtained by Rupe and Steinbach from curcumone (*Ber.*, 1910, **43,** 3465) and by Jackson and Menke (*Amer. Chem. J.*, 1884, **4,** 81) by oxidising turmerol with potassium permanganate ($C_{11}H_{14}O_2$; m.p. 34–35°) are probably impure specimens of curcumic acid. The sesquiterpene ketones occurring in the oil as well as curcumone yield the same curcumic acid, indicating that one of the ketones contains the structure 

The fraction 152–165°/10 mm. (88 per cent. ketone as $C_{15}H_{22}O$) gives about 70 per cent. yield of curcumone showing that the main bulk of the sesquiterpene ketones is converted into curcumone. The analysis of the ketone fractions and titration with bromine showed the presence of a mixture of ketones $C_{15}H_{22}O$ and $C_{15}H_{20}O$. Semicarbazones, oximes, and dinitrophenylhydrazones were all obtained as liquids. The secondary alcohol obtained by reduction of the ketones by sodium and alcohol was also found to be a mixture. No solid derivatives characterising any of the alcohols were obtained.

The oxime of the sesquiterpene ketones was only partially soluble in ether, the remainder being soluble in chloroform. Both the ether and chloroform soluble oximes contained 6·3 per cent. nitrogen, $C_{15}H_{22}NOH$ and $C_{15}H_{20}NOH$ requiring 6·0 and 6·1 per cent. respectively. The amines obtained from these oximes by reduction with sodium in alcoholic solution were different from each other, one of them giving a sparingly soluble oxalate—$C_{15}H_{21}NH_2.H_2C_2O_4$ (m.p. 130°).

The liquid semicarbazone was not hydrolysed by 2 per cent. sulphuric acid or oxalic acid in the cold but on boiling with oxalic acid, 25 per cent. of the semicarbazone decomposed giving a ketone mixture consisting of 65 per cent. curcumone and 35 per cent. of a ketone $C_{15}H_{22}O$. The larger portion (75 per cent.) of the semicarbazone was unaffected by concentrated oxalic or hydrochloric acids. The semicarbazones obtained at the laboratory temperature or by boiling on water bath were identical in their behaviour.

EXPERIMENTAL.

The crushed rhizomes (90 lbs.; moisture 9·2 per cent.) were distilled in steam yielding an oil (4·76 lbs.; 5·8 per cent.) of a lemon colour and aromatic odour. Another consignment yielded 6·3 per cent. on the dry roots. The oil was dried over anhydrous magnesium sulphate and had the constants given in Table I which also includes the values observed by previous investigators.

TABLE I.

	Bangalore	Rupe[1]	Jackson[2]	Bacon[3]
$d^{30°}_{30°}$	0.9245	..	..	0.930
$d^{20°}_{20°}$	0.9290	0.9388	0.9539	..
$n^{30°}_{D}$	1.5064	..	..	1.5030
$[a]^{30°}_{D}$	−17.3°	−24.8	−24.6	+8.6
Acid value	0.8	..	..	..
Ester value	3.2	..	..	81
Acetyl value	26.3	..	..	..
Ketones as $C_{15}H_{22}O$	58.1	..	..	..
Phenols	..	..	..	..

The ketones were estimated by the oximation process of Stillman and Reed (*loc. cit.*). The latter consists in estimating the excess of hydroxylamine left after oximation of the ketone, by titrating with hydrochloric acid using bromo-phenol blue as indicator.

Free acids.—The oil (1600 g.) was dissolved in ether (3000 c.c.) and the solution shaken with 2 per cent. sodium carbonate solution (600 c.c.). The alkaline layer was removed, acidified with dilute sulphuric acid and distilled in steam. The oil that separated had a fatty smell and was dried and titrated against standard alkali (0.2135 g. required 22·5 c.c. NaOH (0·087 N), equivalent 108·9) which indicated a mixture of valeric and caproic acids.

Acids present as esters.—The oil (500 g.) recovered from the last experiment was boiled with alcoholic potassium hydroxide (3 per cent.), poured into water and extracted with ether. The alkaline solution was evaporated to a small bulk, acidified with dilute sulphuric acid and distilled in steam. The silver salt was prepared from the distillate after neutralisation with ammonia (Found: Ag, 51·3; silver valerate requires Ag, 51·7 per cent.).

Distillation of the oil.—The oil (1000 g.) which weighed 993 g. after treatment with 2 per cent. sodium carbonate, was distilled under

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[1] *Ber.*, 1909, **42**, 2516.

[2] *Loc. cit.*

[3] *Philippine J. Sci.*, 1910, **5A**, 262.

diminished pressure (20 mm.) with a 4-pear Young's column, the following fractions being obtained:—

TABLE II.

Fraction	B.P.	$d_{30°}^{30°}$	$n_D^{30°}$	$[\alpha]_D^{30°}$	Weight in g.	Yield per cent. on original oil
1	60– 80°	0·8559	1·4682	+75·7°	16·0	1·6
2	80– 85	0·8612	1·4731	+66·5	5·0	0·5
3	85– 90	0·8714	1·4758	+54·7	4·0	0·4
4	90–100	0·8802	1·4769	+27·7	2·0	0·2
5	100–110	0·8841	1·4774	+22·9	1·5	0·2
6	110–125	0·8911	1·4784	+14·8	1·5	0·2
7	125–140	0·8975	1·4802	– 7·5	4·0	0·4
8	140–145	0·9041	1·4836	–29·1	46·0	4·6
9	145–150	0·9075	1·4982	–42·4	37·0	3·7
10	150–155	0·9164	1·5013	–32·3	152·0	15·2
11	155–160	0·9287	1·5037	–29·0	103·0	10·3
12	160–165	0·9344	1·5072	–26·1	131·0	13·1
13	165–170	0·9430	1·5097	–22·5	143·0	14·3
14	170–175	0·9469	1·5111	–18·3	144·0	14·4
15	175–180	0·9481	1·5141	–10·7	178·0	17·8

In the accompanying graph in Fig. 1 curves are drawn by plotting the physical constants, *viz.*, boiling points, specific gravities, refractive indices and rotations against the percentage yield of the oil. The yield of the lower boiling constituents is comparatively small, for all the curves rise abruptly until they reach about 11 per cent. yield and then gradually deflect towards the abscissæ. The optical rotation curve contains four or five zones.

Fraction 1 (*d-sabinene and d-α-phellandrene*).— No semicarbazone or urethane could be obtained from this fraction. It was distilled over sodium twice and had then the following constants: d_{30}^{30} 0·8522; n_D^{30} 1·4668; $[\alpha]_D^{30}$ +80·4°. On oxidation with alkaline permanganate a small quantity of *d*-sabinenic acid was obtained melting at 55–56° which was unaltered when mixed with an authentic specimen.

The fraction also yielded an appreciable quantity of a nitrite when treated with sodium nitrite and acetic acid in petrol ether solution. It was recrystallized from aqueous acetone and melted at 112–113°, 0·1038 g. dissolved in 10 c.c. chloroform had $\alpha_D = -1·3°$; $[\alpha]_D = -125°$; *d*-α-phellandrene nitrite, according to Wallach, melts at 113° and has $[\alpha]_D = -138°$.

Fractions 2–6.—They were mixed and refractionated twice with a Young column at 20 mm. when the following fractions were obtained:

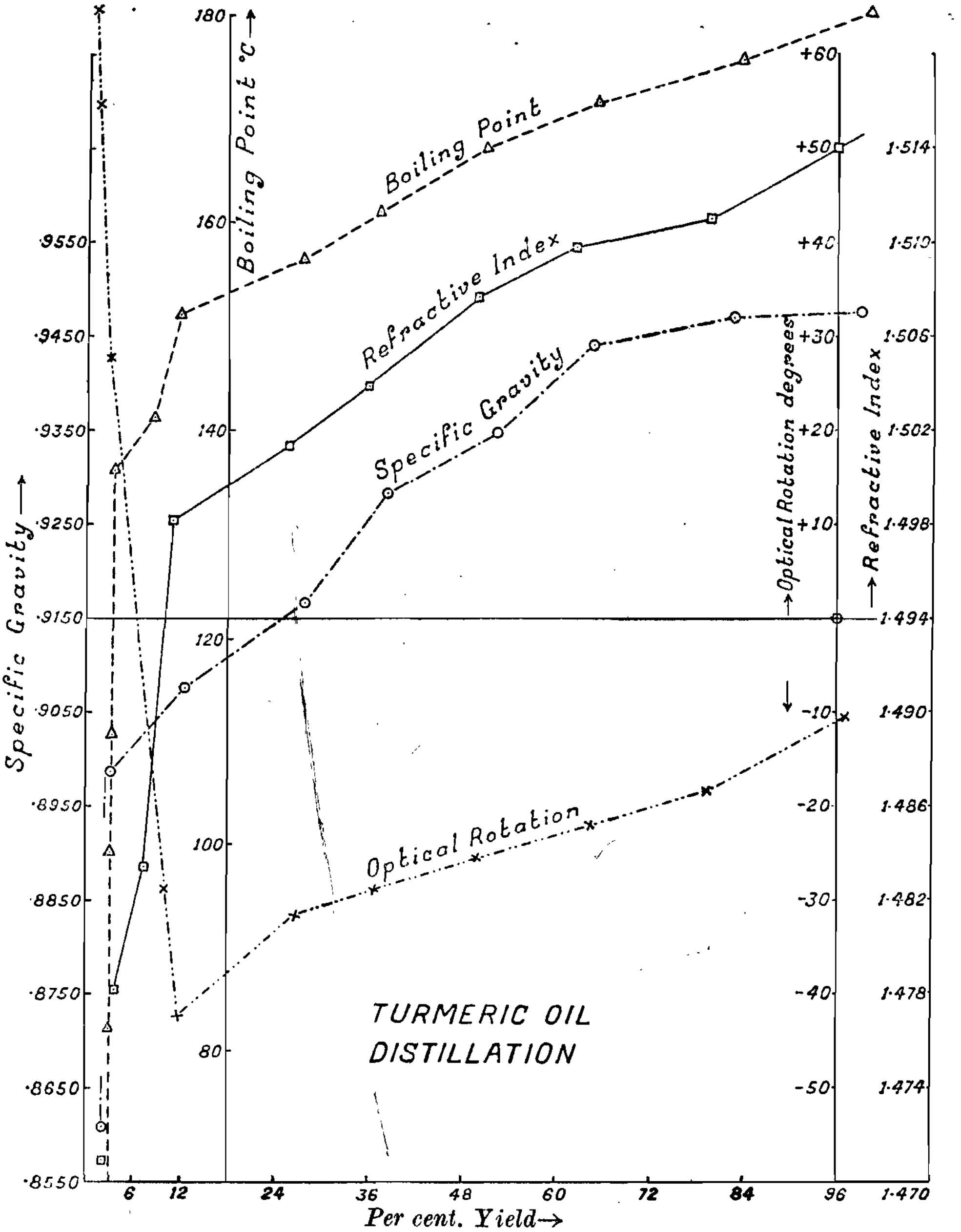


Fig. 1.

TABLE III.

Fraction	B. P.	d^{30}_{30}	n^{30}_{D}	$[a]^{30}_{D}$	Weight in g.	Yield per cent on original oil
A	– 70°	0·8746	1·4687	+46·2°	3·0	0·3
B	70–115	0·8991	1·4795	–13·9	3·0	0·3
C	115–130	0·9005	1·4659	–27·3	4·0	0·4

They all had a marked camphoraceous odour. Each of them yielded a yellowish white precipitate on triturating a well-cooled solution in petrol ether with concentrated phosphoric acid showing the presence of cineol.

Fraction C (*Borneol*).—Since from the constants an alcohol was suspected, the fraction (1 g.) was treated with an excess of phenyl isocyanate, when on standing a crystalline urethane was deposited. It was freed from diphenylurea with light petroleum and was recrystallized from dilute alcohol when needles melting at 137–138° were obtained. The identity of this substance with the phenylurethane of borneol was proved by the method of mixed melting point.

Fractions 7–11 were repeatedly refractionated at 5 mm. and fractions which appeared to be mainly sesquiterpenes were mixed and distilled over sodium when the fractions given in Table IV were obtained.

TABLE IV.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	$[R_L]_D$	Weight in g.	Yield per cent. on original oil	Carbon	Hydrogen
D	115–117°	0·8677	1·4935	–38·4	68·4	15·0	1·5	88·15	11·71
E	117–121	0·8691	1·4937	–59·2	68·4	85·0	8·5		
F	121–123	0·8695	1·4938	–47·4	68·4	50·0	5·0		
G	124–127	0·8734	1·4941	–26·5	68·0	30·0	3·0		
H	127–131	0·8742	1·4942	–22·0	68·0	15·0	1·5		

Fractions D–H (*Zingiberene*).—The physical constants of these fractions do not vary very widely and the differences are probably due to other sesquiterpenes and perhaps traces of sesquiterpene ketones, since the values of $[R_L]_D$ are very constant. Fractions D, F and H gave a nitrosochloride with amyl nitrite and hydrochloric acid melting at 96° (mixed m. p. 95–96°) after crystallisation from a mixture of ethyl acetate and alcohol.

Zingiberene dihydrochloride.—Fraction E (10 g.) was dissolved in glacial acetic acid (50 c.c.) and through the well-cooled solution, a brisk current of dry hydrogen chloride was passed until the solution was saturated. On pouring into water, isozingiberene dihydrochloride (4·3 g.) was obtained melting at 168-169° after recrystallisation from ethyl acetate (Found: Cl, 25·8; $C_{15}H_{26}Cl_2$ requires Cl, 25·6 per cent.).

Zingiberene nitrosate.—Fraction E (5 g.) yielded (1·2 g.) nitrosate melting at 86–87° after recrystallisation from ethyl acetate (Found: C, 60·71; H, 8·02; N. 9·3; $C_{15}H_{24}N_2O_4$ requires C, 60·81; H, 8·11; N, 9.46 per cent.).

Zingiberene nitrosite.—Fraction E (5 c.c.) dissolved in petroleum ether (40 c.c.) was mixed with a saturated solution of sodium nitrite and glacial acetic acid (4 c.c.) gradually added and allowed to stand. The crystals which separated melted at 96–97° after crystallising from methyl alcohol. The physical constants and the formation of these derivatives left no doubt as to the sesquiterpene fractions being mainly composed of zingiberene.

The residue (140 g. ; Table IV) with fractions 12–15 (Table II) were mixed and fractionated at 12 mm. twelve times using a 16″ Widmer column, mixing together fractions having the same physical properties, the fractions in Table V being obtained.

TABLE V.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{5780}$	$[\alpha]^{30}_{5461}$	$\frac{[\alpha]^{30}_{5461}}{[\alpha]^{30}_{5780}}$	Weight in g.	Yield per cent. on original oil
a	150–152°	0·9226	1·5024	–26·8°	–33·2°	1·24	90	9·0
b	152–154	0·9250	1·5029	–28·4	–35·8	1·26	82	8·2
c	154–156	0·9317	1·5047	–29·4	–35·7	1·21	20	2·0
d	156–157	0·9358	1·5065	–28·3	–32·1	1·13	15	1·5
e	158–159	0·9378	1·5074	–30·4	–34·2	1·13	24	2·4
f	159–160	0·9445	1·5094	–27·3	–30·7	1·12	21	2·1
g	160–161	0·9448	1·5101	–26·3	–29·9	1·13	27	2·7
h	160–161	0·9448	1·5105	–26·1	–29·3	1·12	25	2·5
i	160–161	0·9448	1·5109	–24·2	–27·3	1·12	36	3·6
j	160–161	0·9458	1·5116	–19·5	–21·4	1·10	27	2·7
k	160–161	0·9461	1·5122	–16·8	–18·4	1·10	51	5·1
l	160–161	0·9466	1·5125	–12·2	–13·5	1·10	11	1·1
m	161–162	0·9469	1·5130	– 8·5	– 8·8	1·03	48	4·8
n	161–162	0·9477	1·5130	– 4·7	– 4·5	0·96	11	1·1
o	162–163	0·9477	1·5135	– 2·6	– 2·1	0·81	12	1·2
p	163–164	0·9479	1·5138	– 0·1	+1·0	..	16	1·6
q	164	0·9499	1·5150	+3·9	+5·3	1·36	25	2·5
r	164	0·9499	1·5150	+7·8	+9·8	1·26	18	1·8

In the adjoining graph in Fig. 2 which shows the relation between physical constants and percentage composition, it is obvious that in spite of repeated distillation, the fractions are still very complex mixtures. It does not seem possible to isolate any pure constituents by fractionation alone. The results obtained by the combustion of some of the fractions are as follows :

Fraction	*a*	*e*	*m*	*o*	*q*	$C_{15}H_{24}O$	$C_{15}H_{22}O$	$C_{15}H_{20}O$
Carbon per cent.	84·1	82·3	82·9	82·8	83·1	81·8	82·6	83·3
Hydrogen per cent.	10·1	10·3	10·2	10·1	9·9	10·9	10·1	9·2
Molecular wt. (by freezing point of benzene)			216		212			

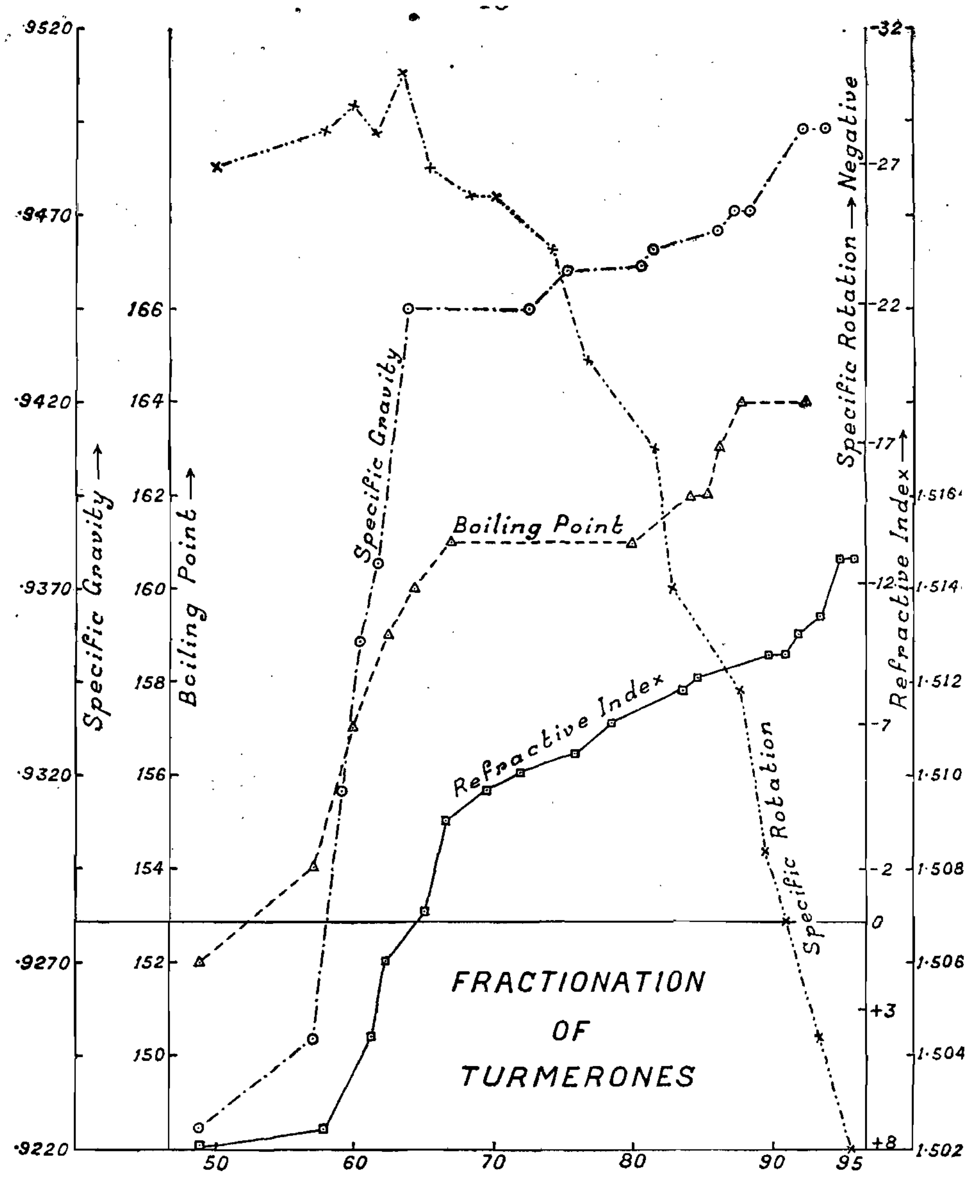


Fig. 2.

The values indicate that the fractions are mainly mixtures o $C_{15}H_{22}O$ and $C_{15}H_{20}O$ compounds. The solution of the fractio *q* (1·042 g.) in carbon tetrachloride required bromine (1·1544 g. dissolved in the same solvent, the excess bromine added being estimate by titration with sodium thiosulphate. From this one finds a molecul of $C_{15}H_{22}O$ or $C_{15}H_{20}O$ takes up 3 atoms of bromine showing that th fraction is probably a mixture of two substances having one and tw double bonds. The main bulk of the oil 158-165°/11 mm. fraction als absorbed about the same amount of bromine.

The fractions *a* and *q* were found to have acetyl values of 10·5 and nil corresponding to 4·1 per cent. alcohol as $C_{15}H_{24}O$ in (*a*). That it was not wholly an alcohol was also confirmed by treating a known weight of the fractions with magnesium methyl iodide dissolved in phenetol and measuring the amount of methane evolved (Hibbert and Sudborough, *J.C.S.*, 1904, **85,** 933). Fraction *m* (0·1365 g.) gave methane (6·3 c.c.) at 31°C and 685 mm. or 2·8 per cent. alcohol as $C_{15}H_{24}O$. Fractions *o* and *q* showed still smaller proportion of the alcohol. On treatment of fractions *a*, *m* and *q* with phthalic anhydride at 130°, no phthalic ester was isolated showing that the alcohols are tertiary.

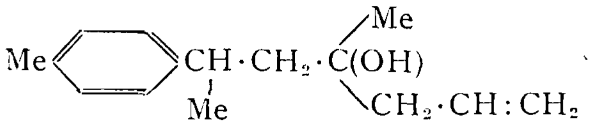
The higher boiling fractions were found to be richer in the carbonyl compounds by Stillman and Reed's method. The fractions *e*, *h* and *m* gave 181·2, 214·0 and 233·4 as carbonyl values corresponding to 71, 84 and 94 per cent. as $C_{15}H_{22}O$. There was no coloration with fuchsine reagent nor did any fraction reduce silver nitrate showing the absence of any aldehyde.

Sesquiterpene alcohols.—The fraction of the oil (500 g.) boiling above 150°/10 mm. with semicarbazide hydrochloride (300 g.) and sodium acetate (300 g.) was boiled in alcoholic solution and allowed to stand for 48 hours and then distilled in steam. An oil (53 g.) was recovered as distillate. This was treated again with semicarbazide and then by distillation in steam an oily distillate (43 g.) was obtained. The latter gave no more semicarbazone and had the following properties: b.p. 102–107°/3 mm., d^{30}_{30} 0·9491; n^{30}_{D} 1·4980; $[\alpha]^{30}_{D}$ −15·2°. To separate the hydrocarbons and other non-alcoholic bodies, the product was benzoylated by Schotten-Baumann's process and the non-benzoylated portion was distilled at 1 mm. The alcohol obtained on decomposing the benzoyl derivative with alkali had the following constants: b.p. 108-110°/3 mm.; d^{30}_{30} 0·9565; n^{30}_{D} 1·4982; $[\alpha]^{30}_{D}$ −14·6°; C, 81·96; H, 10·3; $C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1 per cent. The crude sesquiterpene alcohol was also purified by the boric acid method (*Chem. Ztg.*, 1928, **52,** 898). The crude alcohol (15 g.) was heated with acetic anhydride (15 g.) and boric acid (5 g.) for 5 hours at 120°. The acetic anhydride was distilled at 100 mm. and the sesquiterpenes at 3 mm. The ester was washed with dry ether and decomposed with alkali. The liberated alcohol, on distillation, had the following constants: b.p. 108–112°/3 mm.; d^{30}_{30} 0·9548; n^{30}_{D} 1·4993; $[\alpha]^{30}_{D}$ −12·8°.

The purified alcohol did not react with phthalic anhydride at 130° and was therefore a tertiary alcohol. By Hibbert and Sudborough's method 0·1467 g. yielded 17·3 c.c. methane at 23·5° and 683 mm. showing 7·5 per cent. hydroxyl while $C_{15}H_{24}O$ and $C_{15}H_{22}O$ require 7·7 and 7·8 per cent. hydroxyl respectively. This confirmed that it was not mixed up with ketone and was mainly alcoholic, unlike any of the fractions in Table V.

Curcumone from the sesquiterpene alcohol.—The alcohol (3 g.), 30 per cent. potash (10 c.c.) and ethyl alcohol (10 c.c.) were boiled together for an hour. The reaction product was purified by distillation and gave a benzylidene derivative melting at 105° (mixed melting point with benzylidene curcumone 105°).

Synthesis of an alcohol $C_{15}H_{22}O$.—It appeared possible that an ethylenic tertiary alcohol of the Grignard type (see p. 9) will decompose into curcumone on treatment with alkali. The alcohol



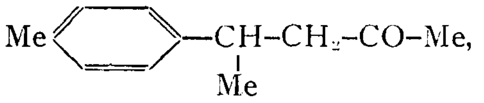
was prepared by the action of magnesium-allyl-bromide on curcumone. The magnesium-allyl-bromide was obtained in excellent yield by Gilman's process (*Bull. Soc. Chim.*, 1928, **43,** 1323; Meisenheimer, *Ber.*, 1921, **54,** 1655) from allyl-bromide (12 g.), magnesium (4·6 g.) and ether (200 c.c.). It was decanted from excess of magnesium into a second flask cooled by an ice-bath and curcumone (10 g.) dissolved in dry ether (100 c.c.) added gradually left overnight and finally boiled for an hour. Ice-water was then added, acidified with dilute sulphuric acid and the liberated alcohol extracted with ether.

A better yield of the tertiary alcohol was obtained by the following process. A solution of allyl-bromide (30 g.) and curcumone (30 g.) in ether (100 c.c.) was added gradually during 2 hours to magnesium (12 g.) suspended in ether (50 c.c.). After about 10 c.c. was added a violent reaction occurred so that cooling with ice was necessary. At the end of the reaction, the mixture was heated for an hour, decomposed with ice and dilute sulphuric acid. The product on distillation gave the following fractions:

Fraction	B.P.	d_{30}^{30}	n_D^{30}	Weight in g.
I	110–140°	0·9376	1·5030	9
II	140–145	0·9511	1·5051	12

On distilling fraction II (5 g.) at ordinary pressure there was decomposition but the distillate gave a semicarbazone (m.p. 125°) identical with that from curcumone. Fraction II (5 g.) was suspended in water (50 c.c.) and 4 per cent. potassium permanganate (110 c.c.) added drop by drop, the solution being maintained between 0 and 5°. The acid formed was recovered and after three days in the ice-chest a few needles appeared (m.p. 39–42°). Fraction II (5 g.), 30 per cent. aqueous potash (8 c.c.) and ethyl alcohol (10 c.c.) were boiled together for two hours on the waterbath. The reaction product distilled at 145–155°/ 7 mm. No derivatives of curcumone could be obtained, showing that the synthetic alcohol is not identical with the sesquiterpene alcohol occurring in the oil. Two more alcohols with the double bond in different positions in the side chain are being synthesised.

Curcumone.—It has been pointed out by Rupe (*loc. cit.*) that the main fraction of the oil boiling above 158°/11 mm. is converted into a ketone curcumone by boiling with an equal volume of 30 per cent. alcoholic potash for three hours. Rupe identified curcumone by its semicarbazone (m.p. 126°) and its benzylidene derivative (m.p. 106°) and confirmed its structure to be



by its synthesis in 1924.

A few of the fractions (Table V) were separately boiled with alcoholic potash for two hours and from the reaction product, semicarbazones and benzylidene derivatives were prepared. The yields of these derivatives from each fraction (5 g.) prepared under similar conditions have been tabulated below:

Fraction ..	*a*	*c*	*e*	*i*	*o*	*r*
Semicarbazone in g. ..	0·2	0·6	1·2	3·8	4·4	4·9
Benzylidene curcumone in g. ..	0·2	0·7	1·8	3·1	5·5	5·6

The semicarbazones obtained from different fractions had the same melting point (125–126°) and were found to be identical with that from curcumone. No semicarbazones melting at 129° or 153° as found by Hintikka (*loc. cit.*) could be isolated. The benzylidene curcumone (m.p. 105-106°) from different fractions was also identical. It is concluded that the higher fractions are richer in the substances yielding curcumone.

To prepare a large quantity of curcumone the fraction 152–165°/10 mm. (200 g., d^{30}_{30} 0·9450, n^{30}_{D} 1·5115, $[a]^{30}$ −18·8°) was boiled with 30 per cent. aqueous potash (180 g.) and ethyl alcohol (225 c.c.) for 6 hours.

The crude curcumone on fractionating twice at 7 mm. gave the following results:

TABLE VI.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[a]^{30°}_{5780}$	$[R_L]_D$	Weight in g.
w	108–112°	0·9430	1·4874	−56·7°		9
x	112–115	0·9426	1·4932	−65·7	54·3	102
y	115	0·9429	1·4949	−56·3	54·5	41
z	115–125	0·9457	1·4980	−15·4		10

Nearly 70 per cent. of the initial fraction is converted into curcumone. The four fractions yielded a semicarbazone identical with that from curcumone. The curcumone is formed not only from the sesquiterpene alcohol which is only about 9 per cent. but also from the sesquiterpene ketones which form the bulk of the oil.

Sesquiterpene ketones.—It has been shown that the main bulk of the oil (b.p. 158–164°/11mm.) consists of sesquiterpene ketones (88 per cent. as $C_{15}H_{22}O$). To remove the alcohols present in the ketone mixture, the fraction (100 g.) was treated with benzoylchloride (50 g.) and 10 per cent. caustic soda (200 c.c.) and shaken for four hours. The reaction product was distilled in steam. The semicarbazone, oxime, phenylhydrazone and *p*-nitrophenylhydrazone were all liquids.

Sesquiterpene ketone semicarbazone.—The oil (100 g.) was mixed with semicarbazide hydrochloride (45 g.) and sodium acetate (40 g.) in dilute alcoholic solution and allowed to stand for seventy-two hours. It was poured into water and the reaction product (118 g.) was distilled in steam. The residue (74 g.) consisted of the mixture of ketone semicarbazones [the ketone $C_{15}H_{22}O$ (59 g.) should yield semicarbazone 75 g.]. When the mixture of oil and semicarbazide was heated for four hours on the water-bath, instead of keeping at the ordinary temperature a solid (m.p. 245°) separated which was found to be hydrazodicarbonamide. The semicarbazone from which the unattacked ketone had been removed with steam had N, 13·3; $C_{16}H_{25}ON_3$ requires N, 15·3, the analytical value for nitrogen is thus too low.

Hydrolysis of the semicarbazones.—The liquid mixture of semicarbazones could not be readily hydrolysed. Both oxalic acid and 2 per cent. sulphuric acid failed to decompose the semicarbazone in the cold. Boiling with phthalic anhydride was also ineffective. The liquid semicarbazone (60 g.) was distilled in steam in presence of oxalic acid (40 g.). An oil (15 g.) was recovered from the distillate having the following properties: b. p. 110–160°/ 7 mm., d^{30}_{30} 0·9477, n^{30}_{D} 1·5040, $[\alpha]^{30}_{D}$ +10·4°. On fractionation at 7 mm. through a packed column (1 ft.), the following fractions were obtained:

TABLE VII.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in g.
K	108–110°	0·9437	1·5000	− 6·0°	1·3
L	110	0·9444	1·5010	+ 0·2	1·5
M	110–112	0·9467	1·5020	+ 7·2	4·3
N	112–145	..	..	..	0·2
P	145–150	0·9544	1·5120	+26·2	3·5

Fractions, K, L *and* M (*Curcumone*).—The constants are in agreement with those for curcumone. The three fractions gave excellent yields of a benzylidene derivative (m.p. 105–106°) and a semicarbazone (m.p. 125°) both identical with those from curcumone. The original ketone liberated from the semicarbazone has apparently undergone decomposition into curcumone as soon as it was liberated in presence of oxalic acid.

Fraction P.—Analysis, C, 82·74; H, 10·12; $C_{15}H_{22}O$ requires C, 82·56; H, 10·09. No benzylidene derivative was obtained showing absence of curcumone. The semicarbazone, oxime and dinitrophenylhydrazone were all liquids. The ketone (1 g.) was boiled with 30 per cent. alcoholic potash (10 c.c.) for an hour. The recovered product gave a benzylidene derivative (m.p. 106°) and a semicarbazone (m.p. 124–125°) showing conversion of the ketone into curcumone. On oxidation of the ketone (2·5 g.) with permanganate (8 g.) in acetone solution an acid (0·4 g.) melting at 42-43° was isolated and found to be identical with curcumic acid by mixed melting point.

The major portion of the semicarbazone of the sesquiterpene ketones was however unattacked by oxalic acid. Both boiling concentrated oxalic acid and alcoholic hydrochloric acid did not decompose the residual semicarbazone. It was recovered by extracting with ether (12 g.), chloroform (6 g.) and alcohol (26 g.).

Reduction of ketone mixture by sodium and alcohol.—To find if the ketones contain conjugated double bonds, the fraction *q* (25 g.) was reduced with sodium and alcohol. After first reduction the specific gravity at 30° fell from 0·9444 to 0·9260 and after four more reductions no further change in properties was observed, the final product giving the following fractions on distillation at 3 mm.

B.P.	d^{30}_{30}	n^{30}_{D}	Per cent. bromine absorbed.
103–105°	0·9129	1·4870	47·8
105–110	0·9181	1·4885	44·5
110–112	0·9192	1·4880	..

The product is a mixture of a saturated and an unsaturated body which could not be separated by distillation. The secondary alcohol $C_{15}H_{28}O$ formed during reduction, was separated by means of the phthalic ester and had the following constants: b. p. 135–140°/10 mm., d^{30}_{30} 0·9156, n^{30}_{D} 1·4854, $[\alpha]^{30}_{D}$ -5·0; C, 80·5; H, 12·8; $C_{15}H_{28}O$ requires C, 80·4; H, 12·5 per cent.).

Oxime.—The fraction 158–165°/10 mm. (100 g., 88 per cent. turmerone as $C_{15}H_{22}O$) hydroxylamine hydrochloride (70 g.) and sodium carbonate (27 g.) in alcoholic solution was boiled together for 3 hours and distilled in steam. The residue (36·5 g.) was extracted with ether and then with chloroform (65·0 g.). Ether soluble oxime contained N, 6·6 per cent. and the chloroform soluble oxime N, 6·6 per cent.; $C_{15}H_{24}NOH$ requires N, 6·0; $C_{15}H_{22}NOH$ requires N, 6·07;

$C_{15}H_{20}NOH$, N, 6·06. The higher content of nitrogen is perhaps due to traces of nitrogen oxides (Nef. *Annalen*, 1900, **310**, 330).

Reduction of ether soluble oxime by sodium and alcohol.—The oxime (10 g.) was dissolved in absolute alcohol (100 c.c.) and sodium (10 g.) added as rapidly as possible. When all the sodium had dissolved, the base was distilled in steam, dissolved in ether and the ethereal extract repeatedly washed with dilute hydrochloric acid. The well-cooled solution of the hydrochloride was made alkaline with sodium hydroxide solution and the resulting oil (3·5 g.) isolated by extraction with ether. The crude base was mixed with excess of an aqueous solution of oxalic acid and the sparingly soluble oxalate which separated was collected; it was obtained as a fine crystalline powder m.p. 130° (Found: C, 66·6; H, 8·7. $C_{15}H_{21}NH_2.H_2C_2O_4$ requires C, 66·4; H, 8·1; N, 4·56 per cent.). No other crystalline derivatives of the base could be obtained.

Reduction of chloroform soluble oxime.—The oxime (10 g.) in absolute alcohol (100 c.c.) was treated with sodium (10 g.). The resulting amine (3·5 g.) gave no crystalline derivative and had the following properties: b.p. 85–95°, d^{30}_{30} 0·9263, n^{30}_{D} 1·4924.

Oxidation of sesquiterpene ketones by dilute nitric acid.—Fraction *q* (20 c.c.) was mixed with dilute nitric acid (1 : 2; 50 c.c.) and gradually heated under reflux for 8 hours. There was a vigorous reaction at 85° and after it subsided, the temperature was raised to 130° when the acid boiled briskly. On gradual addition of more acid (50 c.c.) the brown pasty mass which had been formed, gradually disappeared and a small quantity of white powder was deposited. This was soluble in alkali, with difficulty in sodium bicarbonate and was re-precipitated by acids. It was infusible even at 400°.

The filtrate on concentration and cooling deposited white needles. On triturating with 50 per cent. alcohol, the insoluble portion which separated was purified by sublimation and was confirmed to be terephthalic acid (Equiv. wt., 166; C, 57·7; H, 3·7. $C_8H_6O_4$ requires C, 57·8; H, 3·6 per cent.). The dimethyl ester prepared by refluxing acid (0·5 g.), sulphuric acid (0·5 g.) and methyl alcohol (20 c.c.) melted at 139–140° (mixed m.p. 140°).

The alcohol soluble portion melted at 180° and was found to be *p*-toluic acid (mixed m.p. 180°). The amide melted at 160° (mixed m.p. with *p*-toluamide 159–160°).

On further concentration of the original mother liquor, another crystalline substance was deposited which proved to be oxalic acid.

Oxidation of the ketones by potassium permanganate (curcumic acid).—The oil from fraction *m* (10 g.) was suspended in water (100 c.c.) and to the well-cooled liquid, 4 per cent. $KMnO_4$ solution (500 c.c.)

was gradually added, using mechanical stirring. The neutral bodies were small. The acid portion was purified by distillation in steam. The product (0·7 c.c.) gradually solidified in the ice-chest, needle-shaped crystals (0·38 g.) being obtained. It was recrystallised from methyl alcohol twice when it melted at 42·5–43°. The acid (0·1013 g.) required alkali (7·5 c.c. of ·0755 N) the equivalent being 177·6. It is identical with curcumic acid obtained by Rupe by oxidation of curcumone with sodium hypobromite.

The same acid was obtained in double the yield by oxidising in acetone solution, powdered potassium permanganate (18 g.) being gradually added.

Dehydrogenation with sulphur and selenium.—Fraction *p* (10 g.) heated with sulphur at 180–220° gave a product with the following properties after distillation over sodium, b.p. 140–145°/14 mm. d^{30}_{30} 0·8975, n^{30}_{D} 1·5546, $[\alpha]^{30}_{D}$ $+30{\cdot}8^{\circ}$. No picrate was formed.

Treatment with selenium powder, instead of sulphur and heating at 240–250°, a low boiling hydrocarbon was obtained, b.p. 55–120°/11 mm., d^{30}_{30} 0·8706, n^{30}_{D} 1·4927. Neither cadalin nor eudalin was formed.

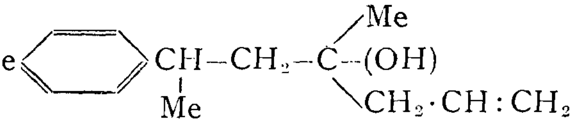
Changes in optical rotation of different fractions of turmeric oil.—During the investigation of the oil, a peculiar phenomenon was observed. The whole oil does not show any pronounced change in the optical rotation but the fractions showed considerable difference in the rotations on keeping. The change in the earlier fractions is from dextro to lævo and in the later lævo to dextro, the two effects nearly balancing each other.

SUMMARY.

1. In addition to *d*–α–phellandrene (1 per cent.) whose occurrence in the turmeric oil was known, *d*–sabinene (0·6 per cent.), cineol (1 per cent.), borneol (0·5 per cent.) and zingiberene (25 per cent.) have been found in the oil.

2. Next to oil of ginger, turmeric oil would appear to be the most suitable source of zingiberene.

3. No alcohol of the formulæ $C_{13}H_{18}O$ or $C_{14}H_{20}O$ appears to be present in the oil. A tertiary alcohol $C_{15}H_{24}O$ or $C_{15}H_{22}O$ which yields curcumone on boiling with alkali is present (9 per cent.).

4. A tertiary alcohol 

$$\mathrm{Me{\cdot}C_6H_4{\cdot}CH(Me){-}CH_2{-}C(Me)(OH){-}CH_2{\cdot}CH{:}CH_2}$$

has been synthesised and its properties studied. It does not yield curcumone on boiling with potash and is hence not identical with the alcohol occurring in the oil.

5. A mixture of sesquiterpene ketones, turmerones $C_{15}H_{22}O$ or $C_{15}H_{20}O$ (58 per cent.) is present in the oil. The semicarbazone, oxime and dinitrophenylhydrazone were all obtained as liquids.

6. The oxidation of the mixture of ketones (turmerones) with potassium permanganate yielded curcumic acid, m.p. 42–43°, identical with that obtained by oxidation of curcumone. On boiling with dilute nitric acid, the ketones gave *p*–toluic, terephthalic and oxalic acids. A small quantity of an infusible acid not identified was also obtained.

7. The secondary alcohol $C_{15}H_{28}O$ formed by reduction of the ketones did not yield any solid derivatives. On oxidation with chromic acid, a ketone $C_{15}H_{26}O$ was obtained which gave a liquid semicarbazone and oxime.

8. No naphthalene hydrocarbon was obtained from turmerones or the secondary alcohols obtained from them by dehydrogenation with sulphur or selenium.

9. Curcumone is not an original constituent of the oil but is formed by the action of alkali on the sesquiterpene ketones and alcohols present in the oil. No other ketones of the type found by Hintikka are formed in this reaction.

10. Appreciable quantities of curcumone were formed from the turmerones by mere boiling with semicarbazide hydrochloride and sodium acetate in alcoholic solution.

11. The mixed semicarbazones of turmerones were only partially (20 per cent.) decomposed by oxalic acid. The ketones obtained consisted mainly of curcumone and about 25 per cent. of another ketone $C_{15}H_{22}O$. The residual semicarbazone could not be decomposed even with alcoholic hydrochloric acid or sulphuric acid.

12. The ketone $C_{15}H_{22}O$ obtained by decomposition of the semicarbazone with oxalic acid gave curcumic acid on oxidation with potassium permanganate.

13. Two oximes were obtained from the turmerone fraction, one soluble in ether and the other soluble in chloroform.

14. The ether soluble oxime gave on reduction with sodium and alcohol an amine $C_{15}H_{23}NH_2$ characterised by a sparingly soluble oxalate $C_{15}H_{23}NH_2 \cdot (COOH)_2$ m.p. 130°. The amine from the chloroform soluble oxime did not give any solid derivatives.

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VI. ESSENTIAL OIL FROM THE RHIZOMES OF *ACORUS CALAMUS*, LINN.

By N. C. Kelkar and B. Sanjiva Rao.

Acorus Calamus, Linn, the sweet flag, one of the oldest known among the spices, is widely cultivated in many parts of the world as it thrives equally well in both temperate and tropical regions. The fragrance of the plant and its oil appears to increase when the climate in which it is cultivated is warmer, and a distinction is made between the commercial varieties from the several countries from which it is obtained. The volatile oil obtained from the rhizomes has been examined by a number of investigators, our present knowledge of the oil being mainly due to the researches of Thoms and Beckstroem (*Ber.*, 1901, **34,** 1021; 1902, **35,** 3187), Von Soden and Rojahn (*Pharm. Ztg.*, 1901, **46,** 243), Semmler and Spornitz (*Ber.*, 1913, **46,** 3700) and finally Russel (*J. Amer. Chem. Soc.*, 1915, **37,** 2387) who examined the oil from various parts of this plant. A preliminary examination of the oil a few years ago from rhizomes grown in India showed that it was not identical with the known European varieties (*Jour. Ind. Inst. Sci.*, 1925, **8A,** 150) and that it resembled the Java oils. It had also superior germicidal properties and hence a re-examination was considered desirable.

It has been found that in the Indian variety the predominating constituent is the phenolic ether, 1.2.5-trimethoxy-4-propenylbenzene called asarone (82 per cent.), terpenes and sesquiterpene derivatives being minor constituents. The usual commercial varieties contain only about 7 per cent. asarone (Finnemore, *The Essential Oils*, 1926, p. 157) and hence the higher proportion of the active constituent should enhance the value of the oil. The characteristic odour of *calamus* is not due to asarylic aldehyde or asarone but to some constituents boiling about 125–135°/11 mm., not so far identified.

EXPERIMENTAL.

On steam-distilling powdered rhizomes (100 lbs.; moisture 13·6 per cent.) an essential oil (2·4 lbs.) was obtained or 2·8 per cent. calculated on the dry rhizomes. The oil was thoroughly dried over anhydrous magnesium sulphate and was found to have the constants given in column 1, Table I, while in other columns, values recorded by other observers are given for comparison. The sample resembles Java oil.

TABLE I.

	Authors	Bangalore[1]	Semmler[2]	Russel[3]	Commercial[1] oil	Japanese[1] oil	Java[4] oil
d_{30}^{30}	1·069	..	..	..	..	..	..
d_{15}^{15}	1·076	1·0694	·9656	0·9583–0·9981	0·958–0·970	0·970 –0·995	1·0783
n_D^{30}	1·5461	..	1·5031	1·5022–1·5172	1·500–1·508	1·5095–1·5175	1·5464
α_D	–1·5°	+5·8°	+27°	+21·7°	+9° to +35°	–12° to +25°	+0·9°
Acid value	2·4	1·4	..	5·1–8·1	0·3	0·2	..
Saponification value	4·1	5·1	..	21·2–50·6	5–20	1–10	12
Saponification value after acetylation	15·7	16·1	..	59·6	30–55	16–28	..
Methoxyl	36·7	..	..	..	..	..	..

Free acids (*palmitic and heptylic acids*).—The oil (730 g.) was dissolved in ether (2000 c.c.) and shaken with 3 per cent. sodium carbonate solution (200 c.c.). On acidifying the latter with dilute sulphuric acid an oily layer separated which on standing partially solidified. The solid acid was filtered, dried and recrystallised from acetone when it melted at 62–63°. It was confirmed as palmitic acid by the method of mixed melting point and determination of equivalent (0·2136 g. acid required 9·6 c.c. of 0·087 N sodium hydroxide, equivalent 256).

The liquid acids were subjected to steam-distillation and the volatile acids fractionally separated. The silver salts were prepared in the usual way after neutralization with ammonia. On ignition the silver salt left silver (45·2 per cent.) which approximates closely to heptylic acid (Ag, 45·5 per cent.).

Phenols (*Eugenol*).—The ethereal solution was then shaken with 2 per cent. potassium hydroxide solution (300 c.c.). The liberated phenol (0·9 g.) had an odour of cloves and gave a green coloration with ferric chloride. It was confirmed as eugenol by the preparation of the benzoyl derivative (m.p. 69°; mixed m.p. 69–70°) by the Schotten-Baumann process.

Acids present as esters (*palmitic and butyric acids*).—The ether was removed and the residual oil was refluxed on the water-bath with 5 per cent. alcoholic potash (200 c.c.) for 3 hours. The acids which separated consisted of palmitic acid (m.p. 62°; equivalent 256·4) and a liquid acid whose ethyl ester had a strong smell of ethyl butyrate.

Aldehydes (*Asarylic aldehyde*).—The oil after treatment with alcoholic potash was shaken with a saturated solution of potassium

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[1] *Jour. Ind. Inst. Sci.*, *loc. cit.*

[2] *Loc. cit.*

[3] *Loc. cit.*

metabisulphite (200 c.c.). The aqueous layer on acidification yielded an oil (0·1 g.) which gradually solidified (m.p. 112–113°; asarylic aldehyde melts at 114°).

Distillation of the oil.—The oil (720 g.) from which phenols, aldehydes and acids had been removed, was fractionated ten times using a 4–pear Young's column in the earlier and a 16 in. Widmer column in the later distillations, the final fractions obtained being as follows :—

TABLE II.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_{5780}^{30}$	$[\alpha]_{5461}^{30}$	$\frac{[\alpha]5461}{[\alpha]5780}$	Weight in grams	Yield per cent. on original oil	Odour	Per cent. asarone
1	70–120°	0·9131	1·4989				0·7	0·1	Camphoraceous	
2	120–125	0·9411	1·5080				0·7	0·1	Calamus like	
3	125–130	0·9661	1·5171	+17·7°	+20·7°	1·17	6·5	0.9	Strong calamus	28·2
4	130–135	0·9663	1·5178	+21·3	+25·0	1·17	5.0	0·7	,, ,,	
5	135–140	0·9965	1·5258	+12·7	+15·1	1·18	7·5	1·0	Camphoraceous	
6	140–145	1·0000	1·5282	+16·2	+19·1	1·18	7·5	1·0	,, ,,	46·0
7	145-150	1·007	1·5313	+15·5	+18·3	1·19	8·0	1·1	Faint	
8	150–154	1·025	1·5357	+10·6	+12·7	1·19	20·0	2·7	,,	
9	154–157	1·068	1·5460	+ 1·8	+ 2·1	1·19	39·5	5·4	Feeble, almost odourless	76·4
10	158–161	1·075	1·5483	+ 1·1	+ 1·3	1·17	42·5	5·8	,, ,,	
11	161–163	1·081	1·5500	+ 0·6	+ 0·7	1·17	36·5	5·0	,, ,,	
12	163	1·083	1·5511	+ 0·2	+ 0·3	1·50	9·0	1·2	,, ,,	79·0
13	,,	1·084	1·5512	,,	+ 0·2	1·00	29·0	4·0	,, ,,	
14	,,	,,	,,	0·0	0·0	..	33·0	4·5	,, ,,	
15	,,	,,	,,	,,	,,	..	55·0	7·5	,, ,,	
16	,,	,,	,,	,,	,,	..	47·5	6·5	,, ,,	81·7
17	,,	,,	,,	,,	,,	..	55·5	7·6	,, ,,	
18	,,	,,	,,	,,	,,	..	53·5	7·3	,, ,,	
19	,,	,,	,,	−0·3	−0·3	1·00	51·0	7·0	,, ,,	
20	,,	,,	,,	−0·5	−0·6	1·20	61·0	8·3	,, ,,	85·1
21	,,	,,	,,	−0·5	−0·6	1·20	25·0	3·4	,, ,,	
22	,,	,,	,,	−1·6	−1·8	1·13	61·0	8·4	,, ,,	82·5
23	,,	,,	1·5502	−1·7	−1·9	1·12	1·5	0·2	,, ,,	
24	,,	,,	1·5491	−2·7	−3·2	1·20	13·0	1·8	,, ,,	78·1

The curves in Fig. 1 connecting the physical constants with percentage composition rise abruptly till 13 per cent.; from 13 to 25 per cent. they are bent towards the abscissæ and from 25 per cent. onwards, are parallel to the abscissæ. The parallel portion corresponds not to pure asarone but to a constant boiling mixture rich in asarone, mixed with smaller quantities of sesquiterpenes and sesquiterpene alcohols. The optical rotation curve is more significant and shows the presence of at least six different constituents.

1.2.5–*Trimethoxy–4–propenyl-benzene* (*Asarone*).—Asarone was estimated by two processes. The methoxyl per cent. by Zeisel's method was found to be 36 in the whole oil while it amounts to 44·7 in pure asarone, showing in the oil an asarone content of 82·6 per cent. The other compounds containing methoxyl are eugenol, methyl-eugenol

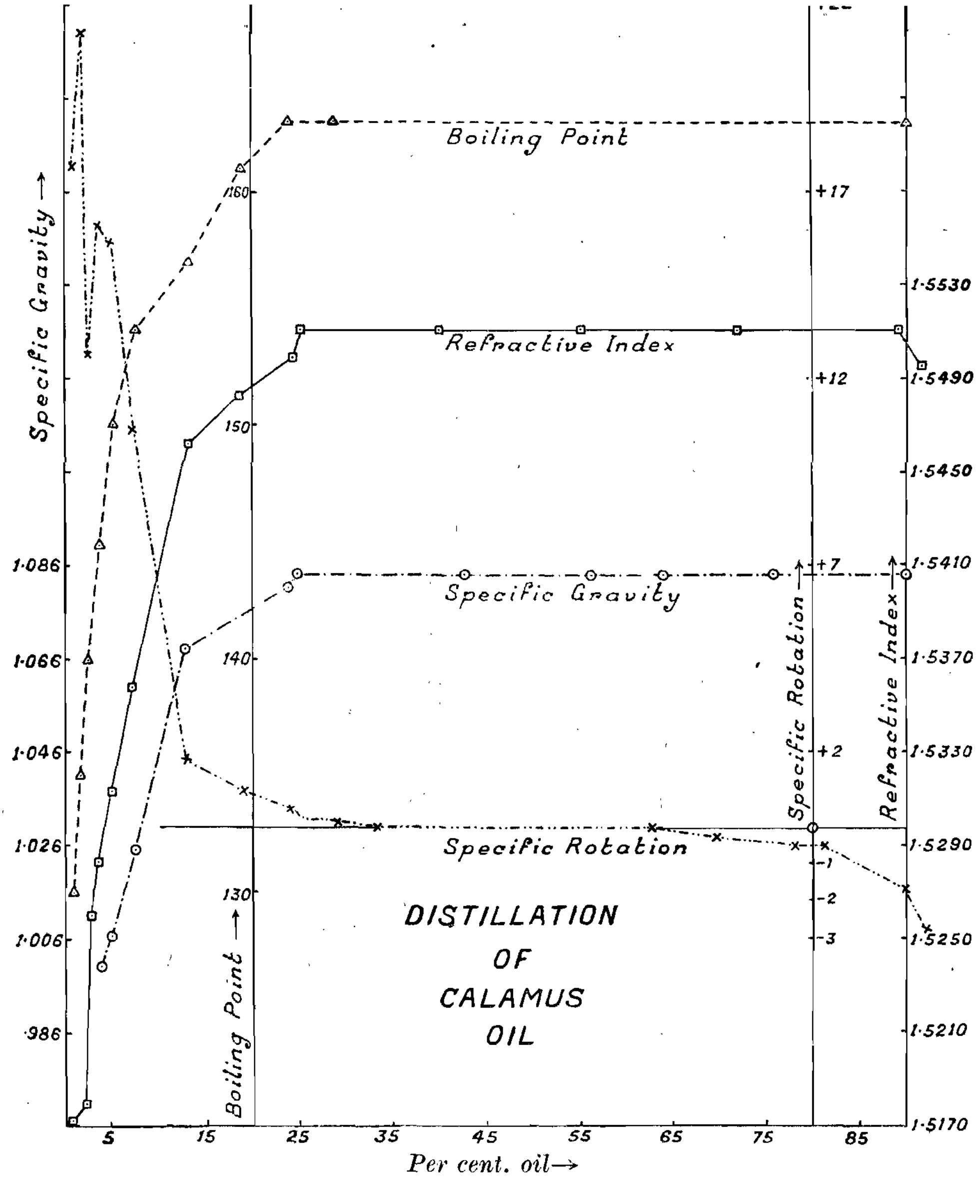

Fig. 1.

and asarylic aldehyde, all of which, however, are present in small amount. The asarone content was also determined directly by polymerisation to *para*asarone and weighing the latter. The oil (10 g.) was cooled in a freezing mixture and 90 per cent. arsenic acid (10 g.) was then added drop by drop, the mixture being kept continually stirred during the addition of the acid. The greenish paste which solidified to a hard mass was treated with cold water to remove excess of arsenic acid. The white sandy powder was then washed with petroleum ether to remove adhering oil. The *para*asarone thus obtained was further purified by dissolving in acetone and reprecipitating with water. It was dried at 100° and then weighed 8·15 g. showing an asarone content of 81·5 per cent. agreeing well with the value obtained by methoxyl estimation. The purified *para*asarone melted at 202–203° agreeing with the figure of Thoms and Beckstroem (*loc. cit.*).

The asarone in the various fractions in Table II was calculated from methoxyl values, 12·7, 20·6, 34·4, 35·6, 36·5, 38·1, 36·9 and 34·9 the corresponding percentage of asarone being given in last column in Table II. The percentage of asarone increases in the higher fractions upto 85 per cent. in fraction 20. None of the fractions yielded any solid asarone on cooling. An attempt to isolate asarone by slow cooling of the fractions from –10° to –25° in an ether bath using solid carbon dioxide only increased the viscosity and the product instead of freezing to crystals gave a syrupy glass-like substance which could be pulled into long threads.

The asarone in fractions 2–8 was converted into *para*asarone by addition of 90 per cent. arsenic acid. The purified *para*asarone (10 g.) was distilled at 14 mm. when a light coloured distillate (3·2 g.) was obtained. The latter solidified on keeping in the ice-chest and was found to be crystalline asarone melting at 62–63° after recrystallising from alcohol (Found: C, 69·1; H, 7·5. $C_{12}H_{16}O_3$ (asarone) requires, C, 69·23; H, 7·69 per cent.).

Asaronic acid.—A solution of potassium permanganate (11·5 g.) in water (150 c.c.) was added drop by drop to the boiling mixture of fraction 20 (5 g.), sodium carbonate (14 g.) in water (200 c.c.) during half an hour. The manganese dioxide was filtered and washed repeatedly with hot water. The filtrate on being washed with ether and acidified, gave a white precipitate (1·7 g.) which after recrystallising from alcohol melted at 143–144°, thus confirming the presence of asarone.

Fractions 1 *and* 2 (*α–pinene*).—The first two fractions on distillation over sodium gave a colourless oil (0·6 c.c.). On treating the fraction (0·3 c.c.) with amyl nitrite and hydrochloric acid, a small quantity of nitrosochloride (m.p. 105°) was obtained. Though the liquid had an odour of camphene, its presence could not be confirmed by any derivatives.

Fractions 3–8 (*Calamene and eugenol-methyl-ether*).—The residual liquid remaining from the mixture of fractions after asarone was removed as *para*asarone gave the following results on distillation at 11 mm.:—

Fraction	B. P.	d^{30}_{30}	n^{30}_D	$[\alpha]^{30}_D$	Weight in grams	C	H
A	–137°	0·9445	1·5094	+23·9	2·0		
B	143–146	0·9566	1·5143	+28·9	5·0	83·3	10·9
C	146–160	0·9851	1·5222	+22·5	2·0		

These fractions reacted very slightly with sodium. Hence they were mixed together and distilled over sodium at 8 mm. twice, the following two fractions being obtained :

Fraction	B. P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in grams	C	H
D	124–129	0·9438	1·5184	+18·1	2·5	86·1	10·7
E	129–132	0·9704	1·5278	+14·5	3·0	78·7	9·1
$C_{15}H_{24}$ requires						88·2	11·8
$C_{11}H_{14}O_2$ (methyl-eugenol) requires						74·2	7·9

The physical constants and the analysis showed that the fractions were not pure hydrocarbons but were mixed with ethers.

When a few drops of concentrated sulphuric acid were added to a glacial acetic acid solution of fraction D, a green coloration was observed indicating the presence of the sesquiterpene calamene (*Apoth.-Ztg.*, 1906, **21**, 879). No nitrosate or hydrochloride was obtained as calamene does not yield any crystalline derivatives. On treating a well-cooled ethereal solution of fraction E (1 g.) with an ethereal solution of bromine (0·5 c.c.) and allowing to stand, a few crystals separated along with an oil which after recrystallisation from alcohol melted at 78–79° showing the presence of eugenol-methyl-ether tribromide (Wassermann, *Ber.*, 1877, **10**, 236).

Fractions 12–18 (*Calamenenol*, $C_{15}H_{24}O$).—These were mixed and treated twice with arsenic acid to separate the asarone completely. The oil, after distilling twice and rejecting the first fraction, had the following constants, b.p. 140–146°/8 mm., d^{30}_{30} 0·9391, n^{30}_{D} 1·5004, a^{30}_{D} +1·8° (Found: C, 82·2; H, 11·2. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent.). It was thus probably a sesquiterpene alcohol.

Fractions 19–22 (*Calameone*).—After removal of asarone from these fractions a yellowish brown oil was obtained. The oil (10 g.) was dissolved in chloroform cooled in a freezing mixture and petrol-ether gradually added with stirring, when, after some time, a brownish pasty substance separated. The supernatant liquid was removed and the deposit was washed a number of times with petrol when a white powder was obtained. After recrystallising four times from alcohol, it melted at 167–168° (Found: C, 75·5; H, 11·1. $C_{15}H_{26}O_2$ requires C, 75·6; H, 10·9 per cent.).

SUMMARY.

1. The difference between the Indian and the commercial varieties of calamus oil is not due to the presence of any new constituents but due to the predominance of asarone in the Indian oil.

2. The Indian oil contains 82 per cent. of asarone while the usual commercial varieties have only about 7 per cent. of the same constituent.

3. The characteristic odour of calamus which appears to be pronounced in the fraction 125–135°/11 mm. is not due to any of the constituents so far isolated from the oil.

4. The percentage composition of the oil is approximately as follows:—a-pinene and camphene, 0·2; eugenol, 0·3; eugenol-methyl-ether, 1·0; asarone 82·0; calamene, 4·0; calamenenol, 5·0; calameone, 1·0.

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THE GAS FROM INDIAN OIL WELLS.

By G. P. Kane, K. R. Krishnaswami and H. E. Watson.

Since the discovery of helium in the natural gas of the Kansas oil-fields by Cady and McFarland in 1907 (*J. Amer. Chem. Soc.*, 1907, **29**, 1524) the presence of this element has been reported in many natural gases (*cf.* Paneth, Gehlen and Pieters, *Z. Anorg. Chem.*, 1928, **175**, 383) but of these, comparatively few have their origin in oil-fields and those that have been examined in Germany and Japan contain only very small quantities of rare gas (Stockfish, *Z. angew. Chem.*, 1928, **41**, 472).

It was suggested by the Director of the Geological Survey of India that an investigation of the oil-gas obtained in large quantities in Assam and Burma might yield results of interest and consequently the following analyses have been undertaken.

As in many cases the gas is not allowed to escape from the wells but retained under high pressure, the securing of samples is a matter of considerable difficulty since special connections have to be made. The samples from Burma were drawn by the Geological Survey of India with the co-operation of the engineers of the Oil Companies and the samples from Assam were sent by the Burma Oil Company directly. We are greatly indebted to those concerned for the trouble they have taken. Most of the samples were in steel cylinders at pressures up to 300 lbs./sq. in., but three were collected over water in Winchester quart bottles and stored in an inverted position.

The origin of each sample is shown in Table I and also the pressure at which it was collected, this figure corresponding with the pressure of gas at the top of the well.

Samples 1–5 were from Burma and the remainder, with the exception of No. 15, from Assam. They were collected at well-distributed points so as to be as far as possible representative for the whole of each field. The last sample was not an oil-gas but natural gas from a spring in the Bombay presidency which was examined for the sake of comparison.

In addition to the determination of helium it was considered of interest to make a complete analysis of these gases and consequently the quantities of carbon dioxide, carbon monoxide, oxygen, nitrogen, hydrogen, methane, ethane and propane were estimated. As methane was the chief constituent, difficulty was experienced in obtaining

TABLE I.

Sources of Gas Samples.

No.	Pressure lbs./sq. in.	Origin.
1	300	Singu B.B.P.C. No. 70.
2	112	Yenangyaung B.O.C. No. 105.
3	34	Yenangyaung B.O.C. Gathering System F. Station.
4	200	Indaw.
5	$\frac{3}{4}$	B.P.C. Well at Payaye.
6	19	Main Line Gas Office.
7	24	Well No. 236.
10	24	No. 4 Collecting Line.
11	29	Well No. 215.
12	..	Well No. 35.
13	..	Well No. 22.
14	..	Masimpur No. 2.
15	..	Gogha, Bombay.

accurate results by absorption methods since it was found that this gas is appreciably absorbed by alkaline pyrogallol, by bromine and by ammoniacal cuprous chloride, while with the higher hydrocarbons the effect is still more marked. Ott (*Montash. Bull. Schweiz. Ver. Gas Wasserfach*, 1925, **6,** 18) had already drawn attention to the absorption of methane by the latter reagent and while the experiments were in progress Pieters (*Z. anal. Chem.*, 1932, **89,** 24) pointed out that pyrogallol absorbs methane and similar gases if it is allowed to remain in contact with the gas when the colour of its solution has changed from brown to violet. As an example, 0·5 c.c. of gases other than oxygen was absorbed from 100 c.c. by 10 c.c. of pyrogallol solution in 1 minute. In the case of ammoniacal cuprous chloride, 15 c.c. of reagent were found to absorb on the average 0·43 c.c. of hydrogen and 1·33 c.c. of methane at each shaking with about 90 c.c. of gas. Special precautions were therefore necessary in making the following experiments.

EXPERIMENTAL.

In the early experiments irregular and low values were obtained for the quantity of higher hydrocarbons present owing to their absorption by the reagents just mentioned, and it was consequently found essential to submit the gas to a preliminary fractionation, a method employed by Burrell and Siebert (*J. Amer. Chem. Soc.*, 1914, **36,** 1537). At the temperature of liquid air, methane is the only hydrocarbon which is evolved from the mixture on pumping and the estimation of oxygen and carbon monoxide can be made with greater accuracy in this fraction than in the original gas.

The absorption of methane was confirmed by shaking 8 c.c. of the pure gas with successive quantities of 5 c.c. of alkaline pyrogallol solution for 3 minutes and measuring the reduction in volume in a Bone and Wheeler apparatus. The quantities absorbed were 0·14, 0·15 and 0·18 c.c. which showed that the absorption was of the same order on each occasion. When absorbing oxygen from the fractionated gas, the process was conducted three times and the mean quantity absorbed in the two last operations deducted from the first figure. Thus, in the case of sample No. 3, four pressure readings were 898·6, 882·6, 874·0 and 864·8 mm. the differences 16·0, 8·6 and 9·2 mm. corresponding with the amounts absorbed and thus the partial pressure of oxygen was 16·0–8·9 or 7·1 mm.

A similar procedure was followed with carbon monoxide and in both cases the constant quantity of gas absorbed at each stage was taken to be methane. This method was not one of very high precision, but it was sufficiently accurate for these analyses. A check on the quantity of carbon monoxide was made in the case of sample No. 2 by passing a known volume of the gas through a U-tube at −120° followed by bulbs containing bromine, potassium hydroxide, sulphuric acid and finally iodine pentoxide, and the liberated iodine was collected in 10 per cent. potassium iodide solution and titrated with N/200 thiosulphate. The amount of carbon monoxide found was 0·36 per cent. whereas the absorption method gave 0·40, a sufficiently good agreement.

The analysis of mixtures of hydrogen and methane with higher hydrocarbons has been discussed by several authors, references to their work being given in a recent paper by MacGillivray (*J. Chem. Soc.*, 1932, 941) which appeared while the present experiments were in progress. Most of these methods require large quantities of gas. Burrell (*Recovery of Gasoline from Natural Gas*, 1925, 80) who has published a large number of analyses of natural gas, in no case records the presence of hydrogen and this is in accordance with our results, only one abnormal sample appearing to contain a trace of this gas. Since the quantity of higher hydrocarbons is also small, solution of methane does not introduce a significant error and in practice it was found that if the gas was cooled to liquid air temperature and the non-condensible portion pumped off, a very sharp separation was obtained. If at the end of the operation the temperature was allowed to rise and the gas was then cooled, condensation was almost instantaneous and no more gas could be removed by pumping.

On replacing the liquid air by a mixture of solid ether and toluene, ethane and propane could be pumped off leaving a residue which was not analysed but designated as ' higher paraffins '. The separation in this case was not quite as sharp as previously but was fairly definite and gave concordant results.

The apparatus used is shown in Fig. 1. It consisted of a constant volume water-jacketted gas burette *A* with two fixed points and a manometer tube *B*. By opening or closing the tap 3 the mercury in this tube could be either exposed to the atmosphere or kept in a vacuum, the latter procedure being adopted when very small volumes of gas had to be measured. *A* was connected through capillary tubing and suitable taps to a syphon *E* for admitting the gas, a bulb *C* for condensation and a small bulb *D* containing oxidised palladium sponge for absorbing hydrogen.

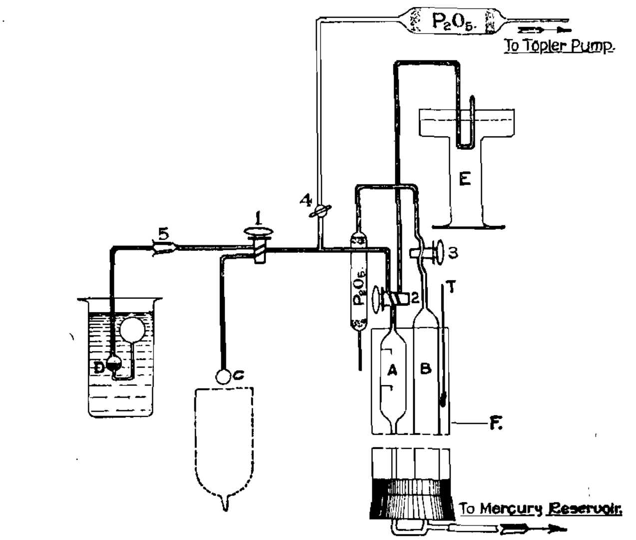

FIG. 1.

To make an analysis the whole apparatus was evacuated by means of a Töpler pump and the gas was introduced into *A* at slightly more than atmospheric pressure. The pressure was measured and the gas compressed into the bulb *C* which was cooled in liquid air. The gas was allowed to expand into *A* and again compressed, the operation being repeated two or three times to ensure thorough mixing, after which the non-condensible portion was pumped off, reintroduced into *A* and measured. The liquid air was then replaced by a toluene-ether bath at −130° and the second fraction removed and measured. Finally *C* was allowed to warm to room temperature and the residual gas pumped off, water being removed by a phosphorus pentoxide tube. As the volume of the burette was rather small (9·4 c.c.) two samples of gas were usually taken for each experiment and the fractions mixed.

The first fractions were tested for hydrogen by passing the gas over the oxidised palladium sponge in *D* which was heated to 100°. The reagent was prepared by heating ammonium palladium chloride to 180° in a current of dry hydrogen until no more hydrochloric acid was evolved, cooling and exposing to air. It was found very reactive when treated with pure hydrogen at low pressure, but in only one case was any diminution in pressure observed when the gases under examination were left in contact with it.

The first fractions were treated in succession with alkaline pyrogallol and ammoniacal cuprous chloride in a Bone and Wheeler apparatus, absorption being repeated three times as already explained. This gave the quantity of oxygen and carbon monoxide. The residual gas consisting of methane with about 10 per cent. of nitrogen required careful treatment to ensure complete combustion. About 2·5 times its volume of oxygen was introduced into the eudiometer and the methane admitted while sparks were passing. Carbon monoxide was always present after this operation and consequently the carbon dioxide was removed with potassium hydroxide and the residue again sparked. This resulted in a mixture of carbon dioxide and nitrogen only. The quantity of methane calculated from the carbon dioxide formed was usually lower than that calculated from the contraction, typical results being :—

	CH_4 from CO_2	CH_4 from contraction
No. 5	85·5	86·5
No. 12	81·5	82·7

This discrepancy arises from the solubility of the carbon dioxide in the sulphuric acid solution used for washing (*cf.* MacGillivray, *loc. cit.*) so that the contraction is too large and the CO_2 measured by absorption is too small. In calculating the results the mean value has been adopted.

The second fraction was treated with potassium hydroxide solution to absorb carbon dioxide and then exploded with excess of oxygen. From the amount of carbon dioxide formed and the contraction, the quantities of ethane and propane could be calculated assuming that only these two gases were present.

It is well known that air is very soluble in liquid methane and is difficult to separate by fractionation. Nitrogen also appears to dissolve readily in solid ethane, since, after applying a correction for traces of nitrogen in the oxygen used for exploding, the second fraction always left a residue of about 5 per cent. of its volume. In most cases this amount was negligible when calculated on the total quantity of gas but in one or two samples in which the amount of ethane and propane was large it was appreciable. If these gases retain nitrogen so tenaciously it seems highly probable that methane is also present in the second fraction and this would result in high values for ethane and low for propane.

In one case (sample 11) in which nitrogen was present to the extent of 31 per cent. the residue was admitted into a tube containing magnesium heated to 550° and maintained in contact until no further contraction took place. The remaining gas, found by its spectrum to be argon, amounted to 0·6 per cent. of the original.

Tests were made for unsaturated hydrocarbons by taking the portion of the gas which could be pumped off at $-130°$ and treating it with bromine in potassium bromide solution. Absorptions of the order of 1 per cent. were recorded but on adding a fresh quantity of bromine an equal amount was again absorbed showing that it was the saturated hydrocarbons which were dissolved or absorbed and that unsaturated hydrocarbons were absent.

Estimation of Helium.

In order to estimate helium, the gas was allowed to remain in contact with charcoal at liquid air temperature until no further absorption occurred and the helium was removed and measured. The apparatus used is shown in Fig. 2.

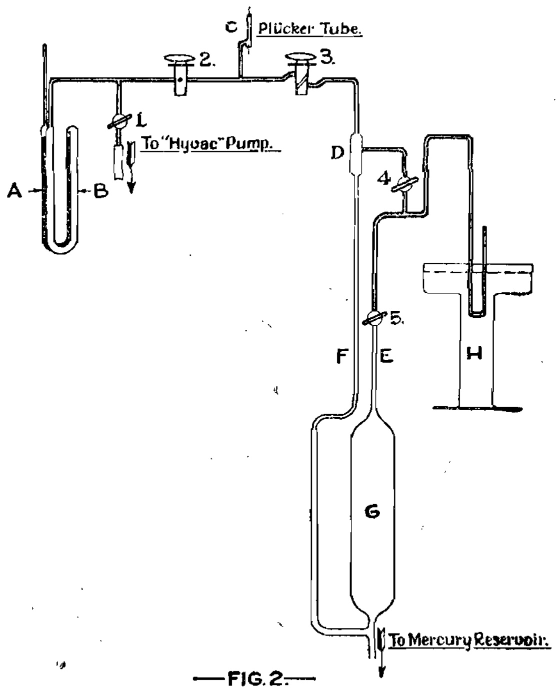

FIG. 2.

Apparatus for the Estimation of Helium.

A is a U-tube containing 4 g. of coconut charcoal and *B* a plain U-tube for condensing higher hydrocarbons. Before starting an experiment these tubes were heated in a sulphur bath and the whole apparatus exhausted. After cooling *A* and *B* in liquid air, the gas was admitted through the tap 4, *G* being previously filled with mercury. To hasten absorption, the whole of the gas on the right-hand side of the apparatus was displaced by mercury as far as the tap 3, the bore of which was also filled with mercury. Since the remaining dead space was constructed of capillary tubing its volume was very small and absorption was complete in about 5 minutes. By closing the tap 5 and lowering the mercury in *G* below the level of the side tube any residual gas diffused into *G* and after compression into the narrow tube *E* which was calibrated, its pressure could be measured. The volume of *G* was known and hence the quantity of gas was determined. The effective volume of the rest of the apparatus taking into account the low temperature of the U-tubes was about 33 c.c. while that of *G* was 140 c.c. so that the total volume of gas was 1·24 times that measured in *E*. This correction was sufficiently accurate in ordinary cases when the volume of gas was very small, but if more precise values were required, the gas after measurement could be displaced through the tap 5 and the residue allowed to enter *G* and be measured as before. Alternatively *G* could be used as a pump and the gas collected in a tube over the syphon, returned to *E* and measured at one time. Since the capillaries used were fine and the tap 5 was very small, there was little risk of loss of gas by this method.

In order to identify and check the purity of the gas, the syphon was closed by the finger or a rubber cap and the gas passed through taps 5 and 4 into the small spectrum tube C made from capillary tubing, the tap 2 being closed. The yellow helium line could usually be seen, but small quantities of impurity from the walls of the apparatus were generally present. These could be removed by cooling the tube leading to the spectrum tube with liquid air when the complete helium spectrum made its appearance. The error in volume caused by this impurity was probably less than the experimental error.

This apparatus was convenient to use and three analyses could be made in one day. 25 c.c. of gas were sufficient for a determination, 0·44 c.mm. giving a pressure of 1 mm. so that 1 part of helium in 100,000 could be readily detected.

RESULTS.

The results found for the different samples are given in Table II which shows the quantities obtained by fractionation and the amounts of the different gases present expressed as percentage on the dry gas. The helium content is in parts per 100,000.

TABLE II.

Sample No.	1	2	3	4	5	6	7	10	11	12*	13	14	15
Volatile at −190°	91·0	89·6	87·7	97·1	96·9	80·2	82·9	73·0	83·4	90·0	84·8	97·8	99·4
Volatile −190° to −130°	7·3	8·1	6·1	2·8	3·1	12·3	10·8	18·0	10·0	9·8	15·2	2·2	0·6
Residue	1·7	2·3	6·2	0·1	0·0	7·5	6·3	9·0	6·6	0·2	0·0	0·0	0·0
Oxygen	0·5	0·8	0·7	0·5	0·4	0·8	1·3	0·5	0·6	0·6	1·3	0·9	1·2
Carbon dioxide	0·3	0·3	0·2	0·5	0·3	0·6	0·4	0·5	0·4	8·4	14·6	1·9	0·6
Carbon monoxide	0·4	0·4	0·4	0·3	0·6	0·4	0·9	0·2	0·6	0·5	0·6	0·4	
Methane	87·0	84·4	69·0	88·2	88·1	75·5	75·7	70·6	51·7	84·5	75·2	80·8	92·2
Ethane	3·8	4·4	2·8	1·7	2·4	7·6	3·0	7·3	3·5	0·6	0·5	0·4	0·0
Propane	3·2	2·9	2·3	0·3	0·1	3·0	6·1	9·5	5·3	0·3			
Higher hydro-carbons	1·7	2·3	6·2	0·1	0·0	7·5	6·3	9·0	6·6	0·2	0·0	0·0	0·0
Nitrogen	3·9	4·5	18·4	8·4	8·1	4·6	6·3	2·4	31·3†	4·8	7·8	15·6	6·0
Helium in 10^5	4	7	0	3	3	1	0	0	3	6	4	7	12

* No. 12 contained 0·1 per cent. of hydrogen.

† Includes 0·6 argon.

The samples from Burma (1–5) with the exception of No. 3 are somewhat similar in composition and contain a high proportion of methane. In Nos. 1 and 2 the excess nitrogen (above the quantity required to form air with the oxygen present) is very small whereas in Nos. 4 and 5 it is 6·4 per cent. The high proportion of nitrogen in sample 3 is abnormal and the higher hydrocarbons are also present in much larger quantity than usual. Of the Assam samples, No. 12, except for its high content of carbon dioxide, resembles the Burmese gases, while No. 11 and in a less degree No. 14 are remarkable for their very high nitrogen content. In No. 13 the amount of carbon dioxide is very large. In Nos. 6, 7, 10 and 11 the ratio of methane to other hydrocarbons is much lower than in the remaining samples. The Bombay gas No. 15 consists of nearly pure methane mixed with air. The amounts of helium have little significance, the proportion of this gas being in most cases of the same order as in air. The results are not in accordance with the suggestion of Cady and McFarland (*loc. cit.*) that the amount of helium varies with the nitrogen-content, there being no correlation between the two quantities. None of the gases contains sufficient helium to render feasible its commercial extraction.

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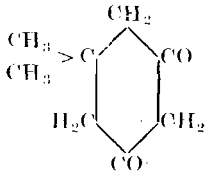
REACTIVITY OF DIMETHYLDIHYDRORESORCIN, PART III.

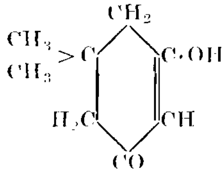
AZO-DYES AND DIAZO-OXY COMPOUNDS.

By B. H. Iyer and G. C. Chakravarti.

The structure of dimethyldihydroresorcin has been represented in two tautomeric forms, (I) and (II).



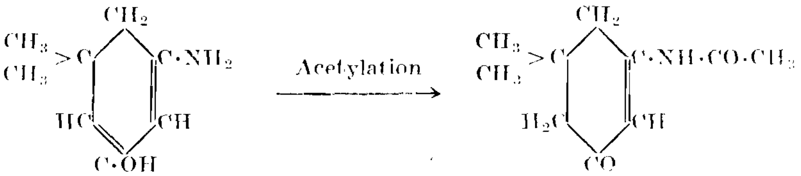
I



II

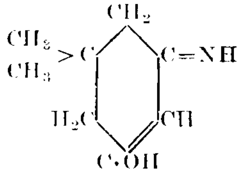
A series of investigations on the reactivity of aldehydes towards dimethyldihydroresorcin has been conducted by Vörlander (*Z. anal. Chem.*, 1929, **77**, 241), Chakravarti, Chathopadyaya and Ghosh (*J. Indian Inst. Sci.*, 1931, **XIV A,** 141) and Iyer and Chakravarti (*ibid.*, p. 157) and the mechanism of the reactions explained on the assumption of structure (II).

Haas (*J. C. S.*, 1906, **89,** 187) condensed dimethyldihydroresorcin with ammonia and various aromatic mono- and di-amines. From his data he maintains that as soon as the hydroxyl group is attacked by a molecule of the base, the other keto group becomes enolised. For instance when the resorcin is condensed with ammonia, 1 : 1-dimethyl-3-amino-5-hydroxydihydrobenzene (III) is obtained. The acetylamino-compound obtained from (III) on acetylation, however, behaves as a ketone (IV).



III IV

From his experiments it would appear that the enolisation was caused by the wandering of a hydrogen atom from the NH_2-group and this wandering was arrested by acetylation, so that the constitution of the amino-compound should more properly be represented by formula (V) and not by (III).

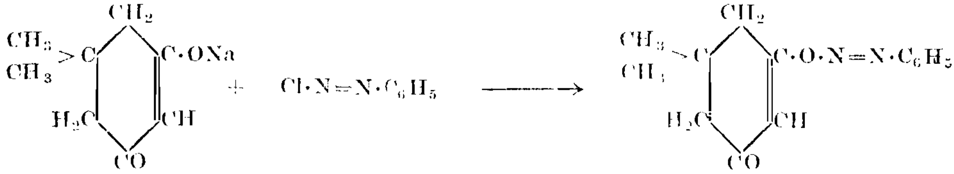


V

Vörlander, and Iyer and Chakravarti (*loc. cit.*) have shown that dimethyldihydroresorcin could react only in the keto-enol form and never in a dihydroxy form as indicated by the work of Haas. Desai's observation (*J. C. S.*, 1932, p. 1081) that the resorcin can give either a C- or an O-alkylated product or a mixture of the two, but never a di-O-alkylated compound lends further support to this view. These considerations proved of sufficient interest to study further the nature of dimethyldihydroresorcin, especially as regards its structure.

Dimethyldihydroresorcin behaves like an acid and so it appeared probable that like phenols it might couple with diazonium compounds to form azo-dyes. As will be evident from the following results, this expectation has been found correct.

When dimethyldihydroresorcin is coupled with phenyldiazonium chloride in an alkaline medium, phenyldiazo-oxydimethyldihydroresorcin (VI) is formed, which is not readily soluble in alkali, the reaction taking the following course:

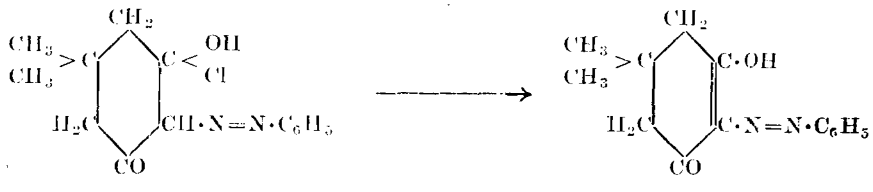


VI

Similar abnormalities have been observed in compounds obtained from phenols possessing strongly acid character (*cf.* Cain and Thorpe, "Synthetic Dyestuffs", p. 54).

When dimethyldihydroresorcin is coupled with phenyldiazonium chloride in an acid medium, phenylazodimethyldihydroresorcin (VIII) is formed. The presence of the hydroxyl group in compound (VIII) is proved by the readiness with which it dissolves in alkali. In another experiment the diazonium salt was coupled with an aqueous solution of dimethyldihydroresorcin. No precipitate separated as long as the reaction mixture was at a low temperature; but on attaining the room temperature and on long standing a small quantity of the compound

(VIII) separated. It may be that the additive compound (VII) first formed loses a molecule of hydrochloric acid to give rise to the azo-compound (VIII).



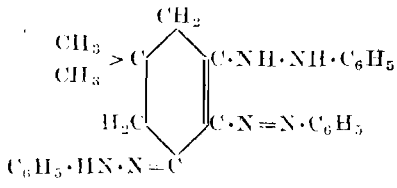
VII VIII

In the case of aniline, and *ortho-*, *meta-*, and *para*-toluidines, the two compounds obtained from acid and alkaline media have the same melting point, remaining undepressed even on admixture. They differ in the diazo-oxy-compound being much the deeper in colour. It appears that in these cases the transformation of the diazo-oxy-compound into the azo-compound is an extremely easy process and is facilitated by heat or treatment with alkali. Similar migration of groups from oxygen to carbon in dimethyldihydroresorcin has been observed by Dieckmann, and Stein (*Ber.*, 1904, **37,** 3379) and by Mameli Efisio (*Gazzella.*, 1926, **56,** 759).

The diazo-oxy and azo-compound obtained from α- and β-naphthyl amines from alkali and acid media respectively show marked difference in their melting points. The O-substituted derivatives are insoluble in alkali and alcohol, whereas the azo-compounds dissolve easily in alkali and can be crystallised from alcohol. In these cases the yields of both types of compounds are very satisfactory.

The easy conversion of phenyl- and tolyl-diazo-oxy-compounds into azo-derivatives and the comparative stability of the naphthyldiazo-oxy-compounds may be due to steric causes.

The azo-compound (VIII) reacts with two molecules of phenylhydrazine to give the phenylhydrazone (IX)



IX

Having obtained these coloured azo-compounds it was thought worthwhile to test their dyeing properties. The process of dyeing was rendered difficult by the insolubility of the dyes in water, but the freshly precipitated substance in aqueous suspension was taken up by woollen fibre with extreme ease. The products resulting from sulphanilic and naphthionic acid were easily soluble in water due to the presence of the sulphonic acid group in the molecules.

On dyeing wool direct from an acid bath bright yellow and red shades could be obtained which improved further on mordanting with dichromate. The dye can also be introduced into silk fibres. In the following table are given the results of a few of the dyeing experiments.

TABLE.

No.	Dye	Material	Direct Dyeing	Mordant Dyeing
1	Phenyl-azo-dimethyldihydroresorcin	Wool	Citron yellow	Canary green
2	*o*-Tolyl-azo-dimethyldihydroresorcin	,,	Lemon yellow	Pea green
3	β-Naphthyl-azo-dimethyldihydroresorcin	,,	Chrome yellow	Canary yellow
4	α-Naphthyl-azo-dimethyldihydroresorcin sulphonic acid	,,	Maroon	..
5	Phenyl-azo-dimethyldihydroresorcin sulphonic acid	,,	Orange vermilion	Terra cotta
6	do.	Silk	Cream	..

Experiments are in progress to synthesise substantive cotton dyes by coupling methone with diazotised benzidine and allied compounds.

EXPERIMENTAL.

Dimethyldihydroresorcin was prepared according to the modified method of Vörlander (*Z. anal. Chem.*, 1929, **77,** 245).

Phenyl-azo-dimethyldihydroresorcin (VIII).—The clear diazonium solution obtained from aniline (4·5 g.) in the usual manner was run rapidly into a solution of dimethyldihydroresorcin (7 g.) in 2*N*-sodium hydroxide (50 c.c.), under mechanical stirring and ice-cooling, and the separated yellow flocculent precipitate allowed to stand in ice for a couple of hours under stirring. In the end the supernatant liquid had an *acid* reaction. The precipitate, after successive treatment with boiling water, very dilute sodium carbonate solution and finally with water, was crystallised from dilute alcohol; m.p. 142°, yield almost quantitative. It was soluble in ether, benzene, chloroform, acetone and methyl alcohol but insoluble in petrol (Found: N, 11·80. $C_{14}H_{16}N_2O_2$ requires N, 11·48 per cent.). The filtrate from the reaction mixture yielded a very small quantity of a red precipitate on basification with caustic soda and this was perhaps the di-azo-oxy-compound.

Phenyldiazo-oxydimethyldihydroresorcin (VI).—The above experiment carried out with dihydroresorcin dissolved in sufficient caustic soda solution to render the reaction mixture definitely *alkaline* yielded a very small quantity of a red precipitate, another crop of which was also obtained from the filtered liquid on salting out. The precipitate after being purified in the manner indicated in the foregoing experiment was crystallised from alcohol; m.p. 140–142° undepressed on admixture with phenylazodimethyldihydroresorcin. Yield very poor. On repeated treatment with caustic alkali the substance gradually goes into solution from which the yellow azo-compound is thrown out by acids. It thus appears that the diazo-oxy-compound is easily transformed into the C-azo-derivative. The final alkaline filtrate yielded a large quantity of the azo-compound on acidification.

o-, m-, *and* p-*Tolyl-azodimethyldihydroresorcin.*—The diazonium solution obtained from each of *o*-, *m*- and *p*-toluidines (5 g.) was added to dimethyldihydroresorcin (7 g.) dissolved in 2*N* caustic soda solution (50 c.c.) and worked up in the manner described under phenylazodimethyldihydroresorcin. The yield was almost quantitative in every case; the products crystallised from dilute alcohol in orange yellow needles.

o-*Tolylazodimethyldihydroresorcin*, m.p. 125° (Found: N, 11·34); m-*Tolylazodimethyldihydroresorcin*, m.p. 122–23° (Found: N, 11·22); p-*Tolylazodimethyldihydroresorcin*, m.p. 156–157° (Found: N, 10·92). $C_{15}H_{18}O_2N_2$ requires N, 10·85 per cent.

p–*Tolyldiazo-oxydimethyldihydroresorcin.*—Diazotised toluidine (5 g.) was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (65 c.c.) containing caustic soda (13 g.), the supernatant liquid reacting strongly alkaline. The small quantity of a red precipitate that had come down was filtered. The filtrate on salting yielded a small additional amount of red precipitate. The final filtrate on acidification yielded a considerable quantity of the yellow azo-compound.

α– *and* β–*Naphthylazodimethyldihydroresorcin.*—Each of α– and β–naphthyl amines (6·7 g.) was diazotised and coupled with dimethyldihydroresorcin (7 g.) dissolved in caustic soda solution (50 c.c.). The products were worked up as in the previous cases.

α–*Naphthylazodimethyldihydroresorcin* crystallised in fine light orange coloured needles from dilute alcohol; m.p. 141° (Found: N, 9·60. $C_{18}H_{18}N_2O_2$ requires N, 9·52 per cent.).

β–*Naphthylazodimethyldihydroresorcin* was not so easily soluble in dilute alcohol as the previous compounds and was crystallised from 95 per cent. alcohol in light orange needles; m.p. 200° (Found: N, 9·65. $C_{18}H_{18}N_2O_2$ requires N, 9·52 per cent.).

α– *and* β–*Naphthyldiazo-oxydimethyldihydroresorcin.*—The diazotised solution obtained from each of α– and β–naphthylamines (6·7 g.) was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (65 c.c.) containing caustic soda (13 g.). The products, after freeing from any unchanged dimethyldihydroresorcin, were further purified by washing with hot absolute alcohol and by precipitating with petrol from benzene solution. They could not be crystallised.

α–*Naphthyldiazo-oxydimethyldihydroresorcin* was obtained as a chocolate-brown precipitate; m.p. above 200° (decomp.) (Found: N, 8·97. $C_{18}H_{18}N_2O_2$ requires N, 9·52 per cent.).

β–*Naphthyldiazo-oxydimethyldihydroresorcin*; m.p. above 255° (decomp.) (Found: N, 9·70. $C_{18}H_{18}N_2O_2$ requires N, 9·52 per cent.).

Phenylazodimethyldihydroresorcin sulphonic acid.—Sulphanilic acid (8·65 g.) was dissolved in 75 c.c. of water containing 3 g. anhydrous sodium carbonate. Sodium nitrate (3·6 g.) dissolved in water (40 c.c.) was added and concentrated hydrochloric acid (15 c.c.) was slowly run in. The diazonium solution thus obtained was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (60 c.c.) containing caustic soda (2 g.). As soon as the two liquids were mixed, a yellow precipitate separated out, the light yellow supernatant liquor having an acid reaction. In an ice-bath at the end of four hours the colour changed from yellow to red. On leaving the mixture overnight, all the solid went into solution which became red in colour and yielded a very small quantity of a precipitate on salting out. The filtrate, after neutralisation with caustic soda, was made slightly acidic and the water was distilled under reduced pressure. The solid residue after drying was extracted with absolute alcohol in a soxhlet apparatus and the yellow product obtained therefrom was crystallised in plates from absolute alcohol; m.p. above 360° (decomp.) with shrinking at 300° (Found: N, 7·54, 7·53; S, 9·04; H_2O, 5·29. $C_{14}H_{16}N_2O_5S,H_2O$ requires N, 8·19; S, 9·36; H_2O, 5·26 per cent.).

When the coupling of diazotised sulphanilic acid was carried out in an alkaline medium, a very tarry product resulted which being much contaminated with the azo-compound as in the previous cases, could not be worked up. Azonaphthyldimethyldihydroresorcin sulphonic acid could not be isolated in a crystalline form. A solution of the crude product was used for the dyeing experiments.

Phenylhydrazones of phenyl- and p-*tolylazodimethyldihydroresorcin.*—A gram each of the substances was dissolved in 50 per cent. acetic acid and heated during 10 minutes on the water bath with two molecular proportions of phenyl hydrazine and the separated solid crystallised from dilute alcohol in fine needles.

Phenylhydrazone (IX) of phenylazodimethyldihydroresorcin was obtained as orange yellow needles, m.p. 191–192° (Found: N, 20·01. $C_{26}H_{28}N_6$ requires N, 19·81 per cent.).

Phenylhydrazone of *p*-tolylazodimethyldihydroresorcin had the same colour and melted at 185° (Found: N, 19·44. $C_{27}H_{30}N_6$ requires N, 19·18 per cent.).

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UTILISATION OF NON-EDIBLE SEEDS AND SEED-CAKES—I.

VEGETABLE CASEIN FROM *PONGAMIA GLABRA* AND ITS APPLICATIONS.

By N. Srinivasan and V. Subrahmanyan.

During recent years, the rapid advance in fat technology has created a widening market for vegetable oils and gained an added importance to the oil-crushing industry. The seed-cake is the most valuable by-product of this industry and its utilisation has been, therefore, the subject of a number of enquiries in different parts of the world, particularly Europe and America.

Although the use of seed-cakes as animal feeds or organic manures is well known, they do not yet command good prices in many parts of India. Even edible cakes often find only limited demand and have to be stored for a considerable length of time as the result of which they become subject to insect and fungus attack and are rendered unfit for animal consumption. If fed to animals, such cakes lead to serious disorders such as inflammation of the digestive organs. The quality of milk and butter are also spoiled. Many of them contain bitter or poisonous ingredients and fetch low prices as organic manures. There are also others, which either possess poor manurial value or are otherwise unsatisfactory, and as such, can hardly have any demand since no use has so far been found for them. In this manner, the producer is generally left with large stocks of cakes which cannot be easily disposed of, so that some other use must be found for them, particularly in India, if the oil-crushing industry is to prove flourishing.

In addition to seed-cakes, there are also large quantities of various kinds of seeds, which are available in tropical forests and for which no satisfactory use, has so far been found. They also contain certain valuable constituents and can be used in the same manner as seed-cakes.

The application of seeds and seed-cakes in different industries does not however find sufficient mention in literature, partly on account of the fact that many of the researches have not been published (being maintained as trade secrets) and partly because the patent specifications relating to the subject are too sketchy for any detailed discussion of the principles and methods involved.

The commoner seed-cakes contain carbohydrates (chiefly starch and cellulose), proteins and other forms of nitrogen, small quantities of unexpressed oil, minerals and in some cases, certain other constituents which render the cakes non-edible. In most cases the protein and starch would appear to be the most valuable ingredients. Many of the seeds and seed-cakes contain over 4 per cent. of nitrogen which corresponds to about 25 per cent. of protein. It is well known that many proteins possess properties similar to those of milk casein, which finds extensive application, in Western countries, in various industries such as paper manufacture, paints and plastics, in the preparation of adhesives, soap, leather, insecticides and a number of other articles of practical utility. Since in many parts of the tropics and particularly in India, the supply of milk is not sufficient even to meet the existing demand as an article of food, it was considered desirable to extract the proteins (vegetable casein) from the different seeds and seed-cakes and to standardise the conditions for their utilisation in the various industries such as those mentioned above. The present communication relates to the seed-cake of *Pongamia glabra* (Vernacular names: Sanskrit, *Karanja* or *Naktamla*; Hindi, *Sukchain*; Bengali, *Dahar Karanja*; Marathi, *Karanja*; Tamil, *Pungam*; Canarese, *Honge*) which is available in fairly large quantities in most parts of India. Some space is also devoted to discussion of the application of vegetable casein in the preparation of paints and plastics and as spreader for insecticidal sprays.

EXPERIMENTAL.

A number of methods have been described and a few patents taken for the preparation of proteins from seeds and seed-cakes. Unfortunately, many of them are of only academic interest, so a number of preliminary trials had to be carried out to select a few that are cheap and convenient to work with.

The first step in the preparation is the extraction of the protein; so the cake, after being sun-dried and powdered to pass the 20 mesh sieve, was treated with a number of solvents which were found from previous studies to be promising. After standing overnight, the supernatant liquids containing the protein in solution were syphoned out in each case, fresh lots of solvent added to the residue and the extraction repeated. After twice repeating the extraction, the mixture of extracts obtained from each treatment was centrifuged to separate the starch and then treated with excess of sulphuric acid or hydrochloric acid accompanied by heating. The protein which then separated was washed, centrifuged repeatedly with water to free it from dissolved impurities, and dried at 55°C in a current of air. The results are presented in Table I.

TABLE I.

Chemical used for extraction	Concentration	Acid used for precipitation	Percentage yield on the dry weight of cake	**Nitrogen** per **cent.**
Lime	Saturated solution of slaked lime	Hydrochloric	7·8	8·1
Lime	Excess of burnt lime	Hydrochloric	Dark product	
Common salt (NaCl)	1 per cent.	Sulphuric	9·8	8·9
(*a*) Common salt and (*b*) Lime	(*a*) 1 per cent. and (*b*) sat. soln.	Hydrochloric	No advantage over NaCl alone	
Caustic soda (NaOH)	0·5 per cent.	Sulphuric	24	7·8
Caustic soda (NaOH)	0·2 per cent.	Sulphuric	15·4	8·5
(*a*) Lime and (*b*) Caustic soda	(*a*) Sat. soln. and (*b*) 0·2 per cent.	Hydrochloric	No advantage over NaOH alone	
Sodium carbonate	1 per cent.	Sulphuric	23	8·2

It may be seen from the above that the hydroxide and the carbonate of soda extract the largest amounts of protein. Sodium chloride peptises only half that quantity but the product obtained by its use is slightly purer than those obtained in other cases. Its merit appears to lie in the fact that it extracts less of foreign matter than the other solvents. Slaking burnt lime together with the cake powder, did not lead to satisfactory results, the protein preparation obtained by that method being dark and impure. Nor was any advantage gained by mixing caustic soda or sodium chloride with slaked lime, so that no saving would result from the use of such mixtures. Caustic soda is nearly twice as efficient as sodium carbonate, but by a repetition of its use for extraction, dark liquors and unclean precipitates were obtained. That alkali would appear to extract, especially after the cake has soaked for some time, a number of foreign substances, so that it will not be so suitable as the yield would appear to indicate. In view of the above and the comparative cheapness of sodium carbonate, it was decided to use that chemical for subsequent extractions.

A further advantage in the use of sodium carbonate is that it can be obtained cheaply in many parts of India in the form of earth salts. Some of the provinces contain fairly large areas of alkaline soils, which, during certain seasons, particularly Spring, form white encrustations containing 10–15 per cent. of the carbonate together with small quantities of the chloride and sulphate of soda. Because of these inorganic impurities and the difficulties in concentration, the efflorescence from such soils is not suited for the manufacture of sodium carbonate. On the other hand, a solution containing a mixture of those salts would be eminently suited for the extraction of protein. The chlorides and sulphates are also protein solvents and would thus form useful supplements to the carbonate. Some experiments carried out with extracts prepared out of alkali soils available near Mandya in Mysore State showed that they were quite as satisfactory as solutions of pure carbonate.

Experiments were next carried out to determine (*a*) the effective concentration and minimum quantity of alkali required for the extraction, and (*b*) the conditions relating to the separation and filtration of the extract, particularly when large quantities of cake have to be treated.

Specimens of powdered cake prepared in the manner described above were extracted repeatedly with alkali solutions of different concentrations. As the result of these trials, it was found that extraction with 1 per cent. solution in the first instance followed by that with 0·5 per cent. solution for successive treatments was quite adequate for the purpose.

With a view to determining the minimum amount of alkali required for the extraction of the protein, some experiments were carried out repeating the treatment with dilute alkali in the manner already indicated. The extracted protein was coagulated by treatment with sulphuric acid followed by heating. The results are presented in Table II.

TABLE II.

Weight of carbonate used for extracting 100 parts of cake	Percentage yield of crude protein on dry weight of cake	Nitrogen per cent. in the preparation
10·0	38·5	5·21
2·0	38·0	5·30
1·5	39·0	5·38
1·0	36·0	5·36

It may be seen from the above that the yields, as also the nitrogen contents of the different preparations, were nearly the same in all the cases. The product obtained by repeated extraction with 10 parts of alkali was found, however, to be dark and hence unsatisfactory for a variety of purposes. The best results were obtained by the use of 1·5 parts of alkali.

After a number of trials, the following was found to be the most efficient method of extraction:—The alkali carbonate corresponding to 1 per cent. of the weight of the cake is dissolved in minimum quantity of water and the cake powder stirred into it to obtain a thick, homogeneous paste. After standing for some time, more water is added until the milky extract begins to separate from the cake. The liquid suspension containing the protein is then separated either by passing through a close-meshed sieve or, preferably, by rotating in a hydro-extractor.

Further observations also showed that prolonged soaking of the cake was unnecessary: in fact such a procedure tended to extract considerable amount of foreign matter. The yields obtained after soaking for different periods of time showed that two hours was quite sufficient for the purpose (Table III).

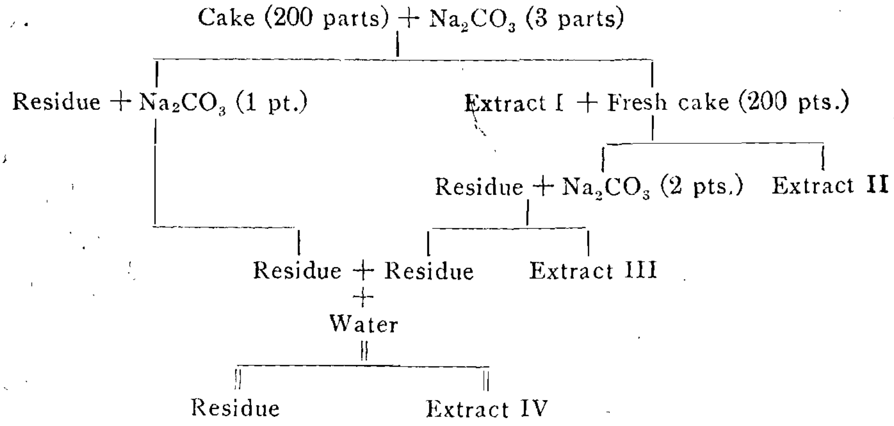
TABLE III.

Liquid soaked in	Time of soaking	Subsequent treatment	Percentage yield on the dry weight of cake	Nitrogen per cent.
Alkali soln.	Overnight	Extracted	38	5·1
Water	,,	Treated with alkali followed by extraction	39	5·2
Alkali soln.	2 Hrs.	Extracted	39	5·4

Some experiments were also carried out powdering the cake to different states of division. It was observed that coarse particles were more satisfactory to work with than fine ones. In the latter case, not only was the filtration more difficult but the protein obtained from the extract was also strongly coloured thereby showing that much undesirable foreign matter was being extracted. Warming the alkaline suspension to hasten the peptisation of the protein was not helpful either, only increasing quantities of colouring matter thus passing into solution. During the heating, part of the starch also got gelatinised so that the subsequent extraction and filtration were rendered difficult.

As the result of a number of experiments the following scheme of extraction (Table IV) was found to be the most satisfactory in practice.

TABLE IV.



Extracts I, II, III and IV were mixed for the precipitation of protein.

In the foregoing scheme, the minimum possible amount of alkali is sought to be utilised for extracting the protein. The concentration of the extract is also maintained as high as possible so that the amount of extract to be dealt with may be small. The disposal of the liquid left after the precipitation of the protein is also thus rendered less difficult.

The efficacy of the above scheme of extraction would be seen from the results of the following experiment:—The cake (500 g.) was soaked overnight in 1500 c.c. of 1 per cent. solution of sodium carbonate. The extract was then separated and the residue re-extracted a number of times with 0·5 per cent. alkali solution. After the fifth extraction, it was found that the coagulable protein in the residue was small, so the extraction was stopped. The mixed extracts were then centrifuged to remove starch, acidified and the coagulation of the protein completed by heating. The results obtained by this method of thorough extraction were compared with those obtained according to the scheme outlined in Table IV.

TABLE V.

Extract Number	Dry weight of protein preparation in grams	Nitrogen per cent. in the preparation	Percentage protein (calculated)
I	93·0	8·0	46·5
II	25·0	6·5	10·0
III, IV & V (mixed)	8·5	5·5	3·0
Total ..	126·5	..	59·5
Results obtained according to Table IV :—			
Combined extract	115	8·2	59·0

TABLE VI.

Composition of the residue left after extraction of protein.

Treatment	Weight of residue in grams	Nitrogen per cent.
Repeated extraction ..	120·0	0·52
According to Table IV ..	143·0	2·1

It may be seen from the above that in spite of the large amount of carbonate (7·0 per cent. on the weight of the cake) used, the method of exhaustive extraction after overnight soaking is less advantageous than the scheme previously outlined. Firstly, although the total amount of protein in the preparation is about the same in both the cases, the one obtained by exhaustive extraction is less pure than that prepared according to the new scheme. Secondly, the residue left after the former treatment is not only less in weight but also contains a lower percentage of nitrogen, thereby showing that a considerable part of the nitrogen passes as non-coagulable matter in the acidulated extract. In view of the above and the convenience in handling the different products in rapid succession, the scheme of treatment outlined in Table IV was followed in all subsequent extractions.

Separation of starch.—The milky extract obtained from the cake contains a fairly large amount of starch which would correspond to over 10 per cent. on the weight of the original cake. Although starch is a desirable ingredient in the preparation of water paints and a few other products, it is not so useful as the protein in other directions. It would be desirable therefore to separate it from the extract before the coagulation of the protein. With this in view, experiments were conducted examining the precipitates separating under different conditions. It was thus found that although starch separates of its own accord (in fact it is the first to separate from the alkaline extract) after standing for about 4 hours, it would be advantageous to separate it by other mechanical means even at the outset. If the spontaneous separation of starch is allowed to proceed, some of the protein is mechanically carried down by the starch and thus lost. A certain quantity also tends to deposit on top of the starchy layer and cannot be easily separated. It was found advantageous, therefore, to separate starch by centrifuging for 15 minutes at a moderate speed of about 1500 R.P.M. The loss of coagulable nitrogen was thus reduced to a minimum as may be seen from the following results (Table VII):—

TABLE VII.

Separation of starch by centrifuging.

Weight of original cake in grams	Dry weight of starchy layer in grams	Nitrogen in the preparation of starch per cent.	Loss of coagulable protein per cent.
500·0	60·0	1·0	5·0

Coagulation of the protein.—This is usually carried out by treating the alkali extract with sufficient amount of acid to render the medium slightly acid. This procedure, though theoretically sound, was not found useful in practice. Firstly, the mineral acid is highly expensive and its use would naturally raise the cost of preparation of vegetable casein considerably. Secondly, the acid required to coagulate the protein is generally very much in excess of what may be expected from the amount of sodium carbonate used for the extraction. The medium is strongly buffered and to attain the optimum hydrogen-ion concentration for the coagulation of the protein, considerable amounts of acid are required. Furthermore, it has been shown in the case of milk casein (Van Slyke and Harts, *Amer. Chem. Jour.*, 1905, **33,** 461; Van Slyke and Van Slyke, *Ibid.*, 1907, **38,** 383; Van Slyke and Van Slyke, *Jour. Biol. Chem.*, 1908, **4,** 259; Linderstrom-Lang and Kodama, *Compt. rend. Lab. Carlsberg*, 1925-27, **16,** 1) that it can absorb and even combine with large quantities of mineral acid especially in presence of the corresponding alkali salts. The vegetable protein would also appear to exhibit a similar behaviour. In one experiment it was observed that to neutralise an extract containing 40 g. of sodium carbonate nearly 60 c.cs. of sulphuric acid (1: 1) were required though the maximum required for the purpose should have been only about 40 c.cs. Moreover, the coagulation was slow and the extract had to be maintained at the optimum temperature (70°C.) for some length of time before any useful separation of protein could take place. Even then, the precipitation was incomplete. Further addition of acid or prolonged heating was useless and, in fact, disadvantageous since the precipitate was observed to deflocculate, and, being finely divided, passed out through the filter. In addition to the above, it was also noted that the preparation of protein obtained by treatment with acid possessed poor adhesive properties and thus became unsuitable for a variety of purposes.

With a view to eliminating the above difficulties and, if possible, to avoid the use of mineral acids, a number of trials were carried out investigating other methods of extraction and precipitation. Some extractions were carried out with either caustic lime or a mixture of sodium hydroxide and slaked lime and followed by passing carbon dioxide to precipitate calcium carbonate together with the protein. The procedure proved satisfactory so far as the protein in the extract was concerned but the extraction itself was rather poor, so the product obtained was mostly calcium carbonate with just a small amount of protein. In view of this inherent defect, the use of lime or mixture of lime and caustic soda was not adopted.

Precipitation of protein by addition of gypsum.—Among the different non-acid reagents that could be used for the neutralisation of alkali carbonate, gypsum appeared to be promising because it is cheap and is abundantly available in many parts of the country. It reacts with the alkali forming the carbonate of calcium which is actually used in the preparation of water paints. Experiments were carried out, therefore, adding varying quantities of gypsum to the alkaline extract and studying the effect on the reaction of the medium and coagulation of the protein. It was observed that addition of a thin suspension of gypsum in water led first to the partial dissolution of that salt in the solution followed by reaction with the alkali carbonate resulting in the precipitation of equivalent amount of calcium carbonate and formation of soluble sodium sulphate. A further quantity of gypsum then passed into solution and reacted with its equivalent of sodium carbonate. In this manner, chiefly owing to the large excess of gypsum and the steady removal of the insoluble calcium carbonate from the sphere of action, the reaction *proceeded forward until the H-ion concentration favourable for* the coagulation of the protein was attained. The precipitation of calcium carbonate also helped mechanically to hasten the separation of the protein. The reactions that led to the partial neutralisation of the alkali and the precipitation of the protein may be represented as follows:

$$\text{(1)}\quad \underset{\text{(solid)}}{CaSO_4} \rightleftarrows \underset{\text{(in solution)}}{CaSO_4}$$

$$\text{(2)}\quad \underset{\text{(in solution)}}{CaSO_4} + Na_2CO_3 \longrightarrow \underset{\substack{\downarrow \\ \text{(precipitate)}}}{CaCO_3} + Na_2SO_4$$

Influence of spontaneous fermentation on the coagulation of protein.—It was observed on certain occasions that the alkali extract of protein left standing for some time turned frothy, suggesting that some fermentation was in progress. It was also noted that in the case of extracts treated with gypsum, the fermentation started even after standing overnight thereby suggesting that the partial removal of the alkali carbonate was helpful to biological activity. With the progress of the fermentation, the frothy extract began clearing accompanied by steady deposition of the protein. The reaction became first neutral and then distinctly acid. These observations suggested that the carbohydrates and other fermentable matter extracted by the carbonate solution were being acted on by the micro-organisms introduced through water, cake, atmosphere and other channels resulting in the formation of acid. In this manner not only was the neutralisation of the alkali carbonate brought about, but the coagulation of the protein also greatly facilitated. The formation of gas (mostly carbon dioxide) was also helpful to the precipitation of protein.

Although a spontaneous fermentation of the above type has its advantages, it was felt, however, that the reactions should be so controlled that (*a*) none of the protein is hydrolysed, and (*b*) the acid production is fairly rapid so that the separation of the protein may be complete within a short period. It was considered desirable, therefore, to use a starter such as a fermentable carbohydrate together with the necessary microflora such as will be provided by a suspension of clay so that the production of organic acids and carbon dioxide may proceed rapidly without appreciably affecting the precipitation of the protein. Since ordinary soil would contain large amount of dark humic matter it was thought desirable to use white clay (kaolin) in its place. Since kaolin is actually used together with casein in certain industries, it was felt that it would make a useful addition to the preparation.

It was observed that the protein separated more readily in presence of small amounts of organic acids, such as those produced by fermentation, than on addition of proportionately larger quantities of mineral acids. With a view to explaining this phenomenon, some experiments were carried out adding different mineral as well as organic acids to suspensions containing vegetable protein and determining the quantities of acids thus taken up in each case. As observed in the case of milk casein (Van Slyke and Van Slyke, *loc. cit.*), the mineral acids were taken up by the protein while organic acids remained practically unchanged thereby suggesting that the protein did not form any complex with organic acids or, having formed one, the product was readily hydrolysed by the water present. This observation would explain the superiority of the biochemical method over that of precipitation by treatment with mineral acid.

With a view to determining the efficacy of molasses as a starter, an experiment was carried out adding it to the alkali extract in quantities corresponding to 1 per cent. on the weight of the cake together with kaolin as the source of mixed microflora for initiating the fermentation. The precipitates, which were formed after standing overnight, were separated by syphoning out the supernatant liquid, centrifuging the suspension containing the protein followed by washing repeatedly with water and finally drying at 55°C. The yield of crude protein thus obtained, as also the nitrogen content, were compared with those for the products obtained by acid precipitation and addition of gypsum respectively. The results are presented in Table VIII.

TABLE VIII.

Method of precipitation	Percentage yield of crude protein on the dry weight of the cake	Nitrogen per cent. in the preparation	True yield of protein as percentage on the dry weight of the cake
Acid (H_2SO_4) ..	38·0	5·3	12·6
Gypsum ..	42·0	5·2	13·7
Biochemical ..	40·0	5·6	14·0

The true yield of protein was calculated by multiplying the yield of crude product with the percentage of nitrogen present in it and dividing the product by 16, which is the average percentage of nitrogen in pure protein. It may be seen from those estimates that the best results were secured by the biochemical method. Treatment with gypsum yielded slightly less and that with mineral acid still less. In view of the above and the comparatively high cost and large consumption of mineral acid, that method was not considered to be satisfactory for the preparation of the protein.

It is not easy to differentiate between the effect of the purely chemical action of gypsum and that of the fermentation which accompanied its addition. Since both the processes help to neutralise the alkali and to facilitate the separation of the protein, it was considered desirable to combine them. Accordingly, gypsum and kaolin were both added as precipitants for subsequent preparations.

The adhesive properties of the preparations obtained by the three methods were compared after mixing them with suitable amounts of clay, chalk and pigment and applying the paints thus obtained to different surfaces. It was observed that the product obtained by acid precipitation would not form a smooth paste that would adhere firmly to any surface. On the other hand, the products obtained by the other two methods mixed more evenly with the added materials and adhered firmly to the surfaces to which they were applied. They also dried readily forming homogeneous films which stood rubbing or washing with water.

It is difficult to explain, at this stage, the nature of the reactions that render the acid precipitated protein so different from the other preparations, in general properties and behaviour. As already indicated, it is probable that the acid, in addition to decomposing the alkali proteinate, also enters into some combination with the liberated protein forming a product with different properties. Some of the acid adsorbed by the precipitate may also become concentrated during the drying and thus affect the quality of the product. Evidence of this may be seen in the partial charring of the acid-treated product on prolonged drying though at a moderate temperature. On the other hand, it would appear that the alkali proteinate is not seriously affected by the other methods of treatment. The medium develops only a mild acidity and the evolution of carbon dioxide hastens the precipitation, so that possibly the composition of the product is less drastically affected by such mild treatments than by heating with excess of mineral acid. This aspect of the problem is of much academic as well as practical importance and further work is in progress to improve on the conditions relating to the precipitation of the protein.

Treatment of the residual cake.—The material left after the extraction of the protein represents about 30 per cent. of the dry weight of the cake and is made up of crude fibre, colouring materials, a part of the starch and the major part of the minerals present in the original cake. It also contains about 2 per cent. of nitrogen which is mostly non-coagulable. The major part of this nitrogen can be brought into solution by prolonged treatment with alkali, but the extract thus obtained also contains large amounts of undesirable colouring matter which greatly reduces the value of the final product. Although it contains small amounts of protein the extraction of the latter is attended by a number of difficulties, so it would appear to be desirable to leave it in the residue and, if possible, find other uses for the same.

If allowed to stand by itself, the residual cake undergoes fermentation, emitting unpleasant odour. It is also overgrown with fungi, which thus cause considerable loss of organic matter and nitrogen. The cake can be rapidly dried however by spreading in thin layers followed by sun drying. If left undisturbed, the dried mass tends to form hard lumps, so it would be desirable to beat out the partially dried product in such a manner as to crumple it to a coarse powder. When the quantity of residue to be dried is large, occasional trampling with feet or treading with wooden shoes will help to break up the lumps and hasten the drying.

The drying of the liquid extract left after the separation of protein is very much more difficult, however, than that of the solid residue. Since the former contains certain valuable ingredients which can be usefully combined with the latter, subsequent experiments were devoted to drying mixtures of the two products.

Concentration of the supernatant liquid.—The liquid residue contains a considerable part of the mineral constituents, as also the bulk of the non-coagulable nitrogen, present in the original cake, together with small quantities of alkali salts of organic acids (formed during fermentation) and sodium sulphate formed through addition of gypsum. The composition of the liquid would suggest that it would be very difficult to dispose of through the usual channels of drainage while the presence of the different fertilising ingredients would point to the desirability of concentrating it in some form and utilising the product as organic manure.

A number of trials were carried out, therefore, treating the liquid in different ways. Evaporation of the thick, syrupy liquid by heating was found to be slow and tedious. The cracking and sputtering of the thick, viscous concentrate rendered heating beyond a point undesirable and even unsafe. Moreover, the final product obtained after prolonged heating was a sticky mass which was highly hygroscopic and was, in consequence, very inconvenient to handle as such. Addition of finely divided clay or such other material was useful but it tended to dilute the final product. It was considered desirable, therefore, to concentrate the liquor upto the syrupy consistency after which the solid, cake-residue could be added to it and the mixed product dried, as a whole, to yield a useful organic manure.

Some experiments were carried out pouring the supernatant liquid into shallow trays and allowing spontaneous evaporation to take place. Small quantities of antiseptics such as phenol or thymol were added to the liquid product to minimise the risk of fermentation and consequent loss of dry matter as well as nitrogen in the gaseous form. In usual practice, however, the antiseptic was not generally needed because the evaporation proceeded rapidly in thin layers so that there was no appreciable loss by fermentation. After the evaporation had proceeded to a point when the residual cake can be added to it, the latter was strewn in carefully, the product worked up to a pasty condition and then allowed to dry in the manner described already. The final product, thus obtained, was clean and dry and possessed no unpleasant odour. Being finely divided, it was more suitable for application to land than the original cake itself. The following observations (Table IX) relating to the yield and composition of the resulting manure will be of interest:—

TABLE IX.

Percentages on the dry weight of the original cake		Percentage composition on the dry weight of final product			
Solid residue	Solids in the extract	Moisture	Organic matter	N	P_2O_5
29·5	17·5	10·1	82·6	4·4	0·6

It was noted that the dry matter contents of the residue and the supernatant liquid were highly variable depending chiefly on the time of soaking with the alkali carbonate and the method adopted for subsequent extraction. Prolonged treatment led invariably to the major part of the cake being peptised by the alkali and thus passing into the supernatant liquid while, with short periods of soaking, the major part of the solid matter, including a high percentage of the non-coagulable nitrogen, were retained in the solid residue.

Further studies on the distribution of nitrogen in the cake showed that although the original computation was made on the assumption that the entire quantity of nitrogen was present as protein, yet no more than 50 per cent. was actually present in that form. Since under the conditions in which the experiments were conducted, all the proteins in the extract should normally have coagulated, it may be inferred that the non-coagulable forms of nitrogen were not really proteins but, probably, intermediary or degradation products thereof. In the present investigation the highest percentage of coagulation secured was of the order of 50 per cent., so it would be necessary to use a different factor $\frac{6 \cdot 25 \times 50}{100}$ to calculate the actual amount of protein present in Hongay seed-cake from the nitrogen content. In a like manner, each seed or seed-cake may have its own factor for protein—the coagulable forms as we understand them—so that it may be useful to conduct further systematic work on this aspect of the problem. The present convention in analytical as well as biological assay is to investigate the coagulated product and then to multiply the results with a factor based on the assumption that all the nitrogen is present in that form. Such an assumption is generally incorrect. Thus, the saline extract of a leguminous seed is not entirely made up of globulins and albumins; only a small portion is present in those forms, while the rest would appear to be made up of less complex, non-coagulable forms of nitrogen. This fact is not taken into consideration however by most workers who assume that the nitrogen is present exclusively as coagulable forms and ignore the non-coagulable ones, which may, in fact, be even more important from the chemical as well as biological point of view. Further research is needed, therefore, to throw light on the nature of the non-coagulable forms of nitrogen present in different plant as well as animal products and to determine their chemical properties and biological values

Some experiments were carried out adding the supernatant liquid to a number of organic materials such as dried leaves and town refuse and allowing the mixture to undergo fermentation to yield a homogeneous compost as the final product. Although this procedure was clean and hygienic and did not require much technical attention, the inevitable loss of dry matter and some of the nitrogen discouraged further attempts in that direction. Moreover, as the operation also took several weeks for completion, it was considered desirable not to add any bulky organic substance, but to prepare a concentrate made up exclusively of the residual solid and the supernatant liquid.

Loss of nitrogen during the preparation of protein.—With a view to determining whether all the nitrogen originally present in the cake was recovered in the form of different finished products, some experiments were carried out studying the distribution of nitrogen at different stages during the precipitation of the protein and the preparation of the manure. After extracting the seed-cake (100 g.) with the requisite amount of alkali, the dry weight of the solid residue as also its nitrogen content were determined. The fermentation of the alkali extract was then initiated by addition of a minute quantity of clay. After two days when the precipitation was complete, the protein was separated and the nitrogen contents of the wet and sun-dried products as also that of the supernatant liquid were determined. The residual cake and a portion of the supernatant liquid were then mixed with a small quantity of clay of known nitrogen content and the product dried rapidly in the sun in the course of a day. The nitrogen content of the resulting manure was then determined. The series of operations outlined above were divided into three groups, (*a*) extraction with alkali carbonate, (*b*) precipitation of the protein, and (*c*) preparation of manure, and the nitrogen balance determined at each stage (Table X).

TABLE X.

Form of nitrogen	Total quantity of nitrogen in grams	Percentage on the nitrogen in the original cake
Extraction with alkali—		
Original cake	4·53	—
Residual ,, ...	0·67	14·8
Alkali extract	3·86	85·2
Precipitation of protein—		
Wet precipitate (148·5 g.)	2·30	50·8
Dry ,, (35·0 g.)	2·30	
Supernatant liquid (500 c.c.) ..	0·83	18·3
Total Nitrogen before precipitation ..	3·86	85·2
,, ,, after ,, ..	*3·13*	*69·1*
Loss of Nitrogen	0·73	16·1

Form of nitrogen	Total quantity of nitrogen in grams	Percentage on the nitrogen in the original cake
Preparation of manure—		
Residual solid	0·67	14·8
Supernatant liquid (350 c.c.)	0·58	12·8
Clay (50 g.)	0·015	0·3
Dry manure (86·5 g.)	1·27	28·0
Total Nitrogen before drying	1·27	28·0
,, ,, after ,,	1·27	28·0

It may be seen from the above that there is no loss of nitrogen either during extraction with alkali or preparation of manure. Quite considerable loss has occurred however during the fermentation of the extract. There could not have been any loss of nitrogen in the coagulable forms (mostly protein) because, as observed in an earlier part of the work, the yield of protein by acid treatment (when no fermentation could have occurred) and by the fermentation method were very nearly the same. In fact, the results (Table VIII) would show that a higher yield of coagulable nitrogen was obtained by the fermentation method than by treatment with mineral acid. It would follow, therefore, that the loss of nitrogen was mostly in the form of non-coagulable matter (mostly intermediary and degradation products of protein) which should ordinarily have passed into the supernatant liquid. As the result of this loss, the nitrogen content of the resulting manure has been lowered by 36·5 per cent.

The loss of nitrogen during the preparation of the protein raises highly important issues which are of much practical significance. Further work is in progress, therefore, to determine the forms in which nitrogen is lost and the chemical and biological mechanism of the attendant transformations. Some preliminary experiments have already shown that the loss of nitrogen occurs mostly, after the first day of the fermentation; and that the loss at the end of 24 hours was only 5 per cent. while that at the end of about 72 hours was 16 per cent. Attempts are also being made to control the conditions relating to the fermentation in such a manner that the precipitation of protein is complete within 24 hours so that the loss of nitrogen may be greatly reduced.

Large-scale preparations of protein.—The cake was crushed to a coarse powder passing the 20-mesh sieve and extracted according to the scheme outlined in Table IV. The extraction was carried out by stirring up the cake in alkali solution of the desired strength and filtering the extract through large metallic sieves. The residue left after the extraction was pressed out thoroughly to remove the liquid retained by it. An alternative procedure that was found to work satisfactorily was that of rotating the alkaline suspension of the cake in a hydro-extractor when the liquid extract was rapidly driven out by the centrifugal force. The extract thus obtained was then treated with the required quantities of gypsum and kaolin, the mixture stirred with long, wooden rods and then allowed to stand.

After two days, when the separation of the protein was complete, the supernatant liquid was syphoned out and the precipitate washed a few times by decantation. The sediment containing the mixture of protein, gypsum and kaolin was dried partly in the sun or partly in a current of hot air at 55-60°. With proper sunshine, the drying was fairly quick, but when the sky was overcast and the weather unfavourable, the drying had to be carried out under shade after first heating the product in a current of hot air for a few minutes. If in spite of the heating the product became smelly indicating further fermentation, it was found useful to treat the drying mass with some antiseptic such as phenol or thymol. The use of inorganic antiseptics—particularly salts of heavy metals—was not found to be useful because they reacted with the protein rendering it insoluble. The antiseptic action was also rapidly lost.

In some cases, it was found advantageous to pass the precipitate repeatedly through a hydro-extractor after addition of necessary quantities of kaolin or other suitable binding material. The centrifugal action combined with the draught of air helps not only to remove the surplus quantity of water but also to dry the product to a stage when it can be spread out on the floor without the danger of fermentation setting in.

The dry product thus obtained is first crushed to a coarse condition and then powdered to a fine state of division passing the 80-mesh sieve. It is then suitable for use as basic material for the preparation of paints, plastics, insecticidal sprays and a variety of other products.

For many purposes such as the preparation of water or oil-bound paints or even the preparation of certain plastics the wet paste can be used as such, adding the necessary pigments and oil or fillers as the case may be. The finished product may be either stored as such or dried, powdered and packed as may be required.

The liquid extract left after the separation of protein is transferred into shallow basins prepared by enclosing requisite areas of earthen flooring with brick and clay borders not exceeding 6″ in height. The rate of drying being dependent on a number of factors, it would be difficult to present a definite estimate regarding the area required for treating extracts from large quantities of cake, but it may be stated that, under favourable conditions, a 20′ square would suffice to dry the concentrated extract from a cwt. of cake, in the course of a bright and sunny day. The nature of the floor, the efficiency of the sub-soil drainage as also the direction of wind are important factors determining the rate of drying the extract. As already indicated, the preparation of enclosures for drying the extract requires no big outlay. Even single rows of half-burnt bricks fixed lengthwise and plastered with clay have been found useful for the purpose.

In fine weather, the evaporation goes on fairly rapidly, so there is no danger of any undesirable fermentation setting in during the drying. In cold and humid weather, the drying is slow in spite of the liquid being exposed in very thin layers. Under such conditions it has been found advantageous to add small quantities of finely divided clay to the liquid so that it works up to a paste. In that condition the concentration of the liquid proceeds rapidly. The paste can also be turned over repeatedly to expose fresh surface from time to time and thus hasten the drying.

To the thick paste, thus obtained, the solid residue left after extraction of the protein is added and the mass turned over a few times. During this operation, a considerable portion of the wet paste forms lumps enclosed within comparatively dry powder. Since such lumps are very difficult to dry, they have to be broken up by beating with wooden rods or treading on with wooden shoes, whichever is convenient, so that fresh surfaces are exposed from time to time. The dry product finally obtained is either stored as such or further dried in a current of hot air—if the weather conditions are unfavourable—prior to storage.

The composition of the finished product is nearly the same as that of the original cake; in fact it is richer in soluble nitrogen and minerals so that its use as a manure would appear to be highly promising. Its manurial value as compared with those of other organic manures is now under investigation and will form the subject of a later communication.

UTILISATION OF VEGETABLE CASEIN IN SOME INDUSTRIES.

Water-paints.—A big branch of the paint trade which has lately been increasing in popularity is the manufacture of water-paints. Such paints are in great demand because of their various excellent qualities combined with cheapness. They are also easily handled and require no special equipment to apply them. They are as convenient to handle as white-washes but are very much superior to the latter in quality.

A preparation of water-paint is made up chiefly of (1) a pigment for covering the surface which is usually chalk, (2) a filler to prevent settling and to make the paint work easily (generally white clay is used for this purpose), (3) a colouring material which may be an earth ochre or a dye for tinting the preparation to the desired colour and shade, (4) a substance (usually starch) to ensure that it will not run on the surface, (5) a binder to hold the different materials together and to fix them to the surface to be painted, and (6) an insolubiliser to convert the film of paint, on drying, into a stable entity that will stand washing with water. Of these, the binder is the most important since it determines, more than anything else, the general quality and the durability of the paint. Several substances are being used as binders but most of them are quite unsatisfactory: in fact the ideal binder is yet to be found. To be satisfactory in every respect, the binder must possess the following qualities:—It must have a good grip on the surface to which it is applied. It should adhere readily to a variety of surfaces, and, having stuck, it should withstand rubbing or mechanical pressure. Thus, it should not scrape off even after vigorous rubbing with the hand. The nature of the binder should be such that it would become insoluble either spontaneously or after some inexpensive treatment. Lastly, the binder itself should be very cheap so that the cost of the paint may be maintained as low as possible. These conditions are not however satisfied by the binders present in the commoner brands of water-paints on the market which contain either water-soluble gums or cooked starch The latter, though otherwise good adhesives, do not stand rubbing or washing with water so that the paints containing them are not much superior to white-washes. The better class paints contain either glue together with paraform or hexamethylene tetramine or milk casein with lime as the insolubiliser. Of these, casein paints are decidedly the most satisfactory with regard to both adhesiveness and stability. Even the best grades of glue assisted by the most efficient treatments for water-proofing do not give such satisfactory products as milk casein. Casein is difficult to peptise, however, so that quite a considerable part of that protein remains undissolved even in presence of dilute alkali. Slaked lime is fairly useful in rendering casein partially soluble, but on exposure to air it absorbs carbon dioxide fairly rapidly so that it soon loses that property. As the result of this, many commercial brands of pastes or powders contain very little caustic lime so that the casein, though present in them, does not serve effectively as the binder. Such paint preparations fail in the hands of the consumer.

In view of the similarity in properties between vegetable proteins and milk casein, difficulties similar to those already mentioned were anticipated and attempts made to overcome them. The conditions for the initial peptisation of the protein were carefully standardised so that, on addition of water, the major part of the material was fairly uniformly dispersed. A number of treatments were also studied so as to facilitate the peptised protein becoming insoluble on standing without, in any way, impairing its properties as an adhesive. A number of paint preparations incorporating the different treatments were then produced and their qualities compared with those of different popular brands available on the Indian market.

In many of the commoner water-paints, the main ingredient is chalk, which is used because of its good covering power. Chalk of good quality is not available, however, in many parts of India, so a suitable substitute has to be found. After some trials, it was found that white clay (kaolin), if properly ground, and mixed evenly with the peptised protein gave as satisfactory results as good grades of chalk. The South Indian kaolin, such as is found in certain parts of Mysore and Travancore, possesses good covering power and can be easily tinted to any desired colour or shade. For the latter purpose, earth ochres cheaply available in many parts of the country were found quite useful. Paints possessing certain unusual shades as also certain bright colours cannot, however, be prepared by using earth ochres alone. For this purpose, it was found necessary to use some insoluble inorganic pigments or aniline dyes.

Some experiments were carried out using lime as the insolubiliser* for vegetable casein. After a number of trials, the following combination was found to be most suitable for the purpose:—A number of mixtures each containing 13 parts of basic material containing the protein together with some starch, gypsum and a small amount of kaolin (originally used as the starter), 10 parts of kaolin with ochre or dye (used for tinting) and 5 parts of slaked lime were prepared and ground into pastes with addition of increasing quantities of water until the desired consistency was attained. Preparations of paint obtained in the above manner were then applied on uniform pieces of wood and the quality of the films compared with those of a few well-known brands of water-paints available on the market. It was observed that the vegetable casein paints dried rapidly, leaving smooth films which could not be easily rubbed off. Second coats could also be applied on top of the dried films without working on the under-coats. The finished paints stood rubbing and washing with water and though some pressure was applied, they could not be easily scraped out. On the other hand, the commercial brands did not stand much rubbing; they also tended to wash off with water so that even on gentle rubbing the entire mass of those paints were removed from the surface.

The foregoing tests having indicated that the preparations of paints obtained with vegetable casein as the binder were of good quality,

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* In the present case, the term 'insolubiliser' is rather misleading because the same chemical has also to function as the solubiliser. Neither milk casein nor the vegetable product can dissolve by itself in water. It has to be brought into solution by some alkali. Lime is the cheapest chemical that can be used for that purpose. The insolubilising action of lime comes only after the paint has been applied to a surface. It absorbs atmospheric carbon dioxide turning into insoluble carbonate. It loses its solvent action on the protein which thus reverts to the insoluble condition. These changes are complete within a few days and the dried film is then enabled to stand rubbing and washing with water.

further trials were carried out applying the paints to a variety of surfaces such as walls, stones, and cement slabs and studying the manner in which the paints adhered to the surfaces, filled up cracks and crevices and stood rubbing and washing. On all such surfaces the vegetable casein paints adhered more firmly, covered up the surface and filled up the crevices more effectively than any of the other preparations with which they were compared.

In many European countries, and to some extent in America, the better class water-paints, particularly those containing casein, are marketed as ready mixed pastes which can be diluted with water to the desired consistency. Such paints, while possessing several advantages, particularly with regard to ease of mixing and high adhesive power, over the dry powder are yet too costly for the average consumer. This is chiefly due to the presence of water which increases the weight of the preparation and the need for using special metallic containers which may sometimes cost even more than the paints. In view of the above and the desirability of producing a preparation which can be mixed with water or oil at the will of the user, some experiments were carried out drying the pastes and storing them as fine, dry powders in paper containers. The drying was carried out at different temperatures with and without using a draft of air to carry away the water vapour. Trials with the powders thus obtained showed, however, although the paints were highly satisfactory as wet pastes, the dry products could not be readily brought into homogeneous suspension: nor did they adhere properly to the surfaces to which they were applied. The dried films came off very easily with rubbing. They were also easily washed away by water. These observations suggested that, during the drying, the binder (the protein) had lost its adhesive property so that the paints obtained from the dry powder were no more than white-washes. It is this difficulty, probably, which precludes the marketing of good quality casein paints as dry powders.

With a view to overcoming this defect, a number of experiments were conducted, adding to the dry paint mixtures different substances which would help to peptise the vegetable casein on wetting with water. Since slaked lime proved unsatisfactory, the use of other chemicals was tried. Caustic alkali and alkali carbonate were both found useful, but the carbonate was found to be more convenient to handle because of its non-hygroscopic character. A number of concentrations of the carbonate were tried as the result of which it was found that 2·0–2·5 per cent. on the weight of the dry paint powder was quite adequate for the purpose.

The following would be a convenient procedure for the preparation of dry paint containing alkali carbonate. The dried protein preparation containing small quantities of starch and gypsum is intimately mixed with the required quantity of sodium carbonate and the mixture ground to fine powder. In this manner, the intimate mixture of the protein and the alkali carbonate would first be ensured. Kaolin is next added and the grinding continued until the mixture forms a homogeneous product. The pigment or mixture of pigments as the case may be, are finally added in quantities necessary to produce the desired colour and shade. The dried powder thus prepared can be kept indefinitely without undergoing any appreciable change. On addition of water, however, the carbonate first dissolves and acts on the protein bringing it into solution. After standing for a few minutes the major part of the finely divided protein passes into solution and the paint is ready for application. By repeated stirring, the peptised protein comes into contact with all the components of the paint and is thus enabled to hold them firmly on setting.

It was observed that the paint prepared in the above manner was rather slow in setting to an insoluble condition. That process can be hastened, however, by adding a small amount of burnt or slaked lime to the alkali carbonate. The carbonate of lime is formed rapidly and thus causes the protein to coagulate more rapidly than might otherwise be the case.

Oil-bound paints.—There is considerable demand for cheap paint materials that would be suitable for covering a variety of surfaces, protecting them against the effects of adverse weather, ravages of insects and fungi, and, at the same time, possessing the water-proofness and other good qualities which characterise the superior classes of oil-paints. The commoner oil-paints are rather costly and consume large quantities of oil which are required not only for the preparation of the paste but also for dilution to the required consistency. Moreover, oil-paints are generally supplied only in the form of ready-mixed pastes which though possessing certain advantages, yet involve the use of special metallic containers. In view of the above, some experiments were carried out preparing oil-bound water-paints with vegetable casein as the binder. As the result of these trials it was found that although the oil could be worked up with the paint material in any proportion, it was not generally possible to dilute such preparations with water without the separation of oil. It was also noted that there is a certain optimum proportion which should be maintained between the quantities of protein, water and oil used in the initial mixture for facilitating indefinite dilution with water at a later stage. The proportion of sodium carbonate to protein preparation also had a decided influence on the suitability of the paint emulsion to stand dilution with water. If the carbonate was below the optimum percentage, the oil tended to separate from the paint thus rendering the distribution inadequate. After a number of trials it was found that a satisfactory procedure would be to first grind up the paint mixture (wet paste) with increasing quantities of oil until a smooth paste could be obtained. A small nucleus of paste containing useful amounts of soap would first be formed which, together with the free carbonate left unused, would soon help to emulsify further quantities of oil upto a maximum which can be determined in each case by actual trial. The oil-bound paste thus obtained would then remain stable and stand dilution with water without any of the oil separating. The diluted paint could also be applied to any surface ensuring satisfactory covering, colour and water-proofness which are characteristic of oil-paints.

It does not appear to be feasible, however, to prepare a dry paint mixture to which indefinite quantities of oil and water can be added. The chief difficulty is the emulsification of the oil which could not be satisfactorily carried out by casual grinding in an ordinary mortar. Careful mixing of the oil, water and alkali followed by prolonged grinding in power-driven mixer is necessary to ensure a good paint mixture which would stand indefinite dilution with water. Further work is in progress to determine whether any of the other emulsifiers could help to bind together the oil, protein and water in different proportions without having to resort to prolonged grinding as in the case of soda. Attempts are also being made to prepare thick emulsions of oil which could be added in any desired quantity to the dry paint powder and could be diluted to any required consistency by mere addition of water. In this manner a dry paint mixture suitable for use either as a water paint or as an oil-bound water paint can be supplied to consumers.

Use of vegetable casein as spreader for insecticidal sprays.—In recent years, the use of chemicals as sprays for the control of insect or weed pests and fungus disease has become increasingly popular. In tropical countries, the spraying of coffee, areca palm and fruit trees has become almost a regular field operation. In actual practice, however, the farmer does not get the full benefit of the sprayed chemical because the latter (*a*) does not, by itself, possess good covering power, (*b*) has no adhesive properties, and (*c*) has the tendency to flake and peel off or get washed out by rain. As the result of this, the spraying operation has to be repeated several times in a season if the pests are to be effectively kept out. The cost of spraying is thus greatly increased without adequate return, so that the need for a cheap spreader that would help to overcome the above defects is now generally recognised.

The possible use of several chemicals as spreaders has been indicated but most of them have proved unsatisfactory in practice. Robinson compared the covering qualities of a number of spreaders and found that proteins were the most efficient, at the lowest concentrations, for the largest number of surfaces tested by him (*J. Agric. Res.*, 1925,

31, 71). Milk casein is known to be fairly efficient and in view of its similarity in properties to vegetable casein and the excellent adhesive quality of the latter, some experiments were carried out using the vegetable casein as spreader for insecticidal sprays. Since the preparation of protein from Hongay seed-cake also contains small quantities of the bitter principle with which the original cake is associated, it was considered that the insecticidal action of the spray would be augmented by the use of that protein.

One part of the crude vegetable casein preparation (Nitrogen 5·6 per cent.) together with 2 parts of copper sulphate (hydrated) and one part of burnt lime were ground together with sufficient quantity of water until a homogeneous paste was obtained. More water was then added, with frequent stirring, to dilute it to a thin suspension corresponding, in strength, to that ordinarily used in field practice. The spray solution thus prepared was compared with standard Bordeaux mixture with regard to both adhesiveness and washability.

The preliminary test consisted in applying uniform drops of the suspensions to the surface of similar pieces of wood and measuring the areas covered by them. After the films had dried the wood pieces were placed under a flowing stream of water and rubbed with the hand to compare their ability to stand the treatment. It was observed that the spots of standard Bordeaux mixture solution (without the spreader) dried after some hours forming relatively narrow circlets which could be easily removed by gentle rubbing. When placed under water, those films washed off readily even without application of pressure. On the other hand, the spots containing vegetable casein dried forming thin and wide circles which adhered firmly to the surface and could not be scraped out by mere rubbing. The films containing the protein also stood washing and could not be removed even after rubbing under water. These observations indicated that the vegetable casein would make a highly useful spreader-adhesive for insecticidal sprays.

Some field trials were next carried out, spraying different kinds of vegetation with suspensions of Bordeaux mixture prepared with and without vegetable casein. It was noted that the plants sprayed with the former were dotted dark blue-green while the latter developed the characteristic light blue spots ordinarily associated with Bordeaux mixture. Even after a few days of drying in the sun, the mixture without the adhesive tended to flake and drop off while no such tendency was observed in the case of the preparation containing vegetable casein. The showers which followed in a few days washed away the little amount of the Bordeaux mixture prepared without the adhesive. On the other hand, the plants sprayed with the suspension containing the protein still carried the entire amount of the spray mixture so that a repetition of the operation was obviated. The heavy rains and the humid weather which succeeded helped further to demonstrate the excellent qualities of the adhesive. Even at the time of writing this paper (six months after the spraying) the insecticide is still in tact on the plants so that further spraying has not been necessary. These results leave no doubt regarding the superior quality of the vegetable casein as a spreader-adhesive.

Utilisation of vegetable casein in the plastic industry.—During recent years, the plastic industry has been gaining considerably in importance and various articles of utility as well as beauty are being manufactured out of natural as well as synthetic products now available on the market. Milk casein is one of the more important substances used in the plastic industry and a large number and variety of articles such as buttons, brushes, combs, umbrella and knife handles, dolls and toys are being manufactured out of it. The world's supply of milk casein is not, however, unlimited so that the possibilities of extending its application are naturally restricted. On the other hand, the vast abundance and relative cheapness of the vegetable product would suggest the possibility of its being not only a supplement but also a useful substitute for milk casein. Its remarkable adhesive properties are already well established. Evidence has also been obtained to show that it sets even at ordinary temperature without much application of pressure. There is no perceptible shrinkage in volume on drying. The finished product is water-proof, non-explosive and non-combustible. These observations would suggest that the vegetable casein has immense possibilities of application in the plastic industry.

Further work is in progress standardising the conditions for the production of vegetable casein on a large scale. Attempts are being made to reduce the cost of the different operations involved and to avoid undue waste of protein and other valuable constituents present in the seed-cake. It is not possible at this stage to present a detailed estimate for the working of a small factory, but small-scale trials with quantities of cake upto a hundredweight of cake have shown that even if the materials used for the preparation of protein are purchased on retail basis, the cost of production of the dried product would be under half an anna (approximately $\frac{1}{2}$*d.*) per pound. It is expected that production on a bigger scale and using cheaper raw materials would further reduce the cost. In view of the abundance of raw material and the low cost of manufacture, it would appear that the vegetable casein has a great chance of standing competition not only with milk casein but also other materials used for similar purpose in the paint or plastic industry.

The processes relating to the manufacture of vegetable casein by the use of gypsum or the biochemical method as also its application in the paint industry and the preparation of insecticidal sprays have been covered by Patents (Government of India, Patent Specification Nos. 20143, 20192, 20193). It is hoped that, with the processes fully standardised, the manufacture of vegetable casein and its use in different industries would prove to be a highly profitable source of business for those interested in the venture.

SUMMARY.

1. The present position with regard to seed-cakes has been discussed and the need for finding new uses, particularly the preparation of vegetable casein, indicated.

2. Among the different solvents that were tried, alkali carbonate was found to be the most satisfactory for the extraction of protein from Hongay seed-cake.

3. The conditions for the extraction of protein have been standardised. Coarsely powdered cake (200 parts) are treated with minimum quantity of alkali carbonate (3 parts) for the complete extraction. The extract is separated by either passing the suspension through a close meshed sieve or, preferably, rotating in a hydro-extractor. The small quantities of starch passing into the extract can be separated by centrifuging.

4. Precipitation of the protein by treatment with mineral acids has been found to be not only wasteful but also unsatisfactory. Higher yield as also better product was obtained by treating the alkali extract with gypsum, kaolin or mixture of gypsum and kaolin and allowing the suspension to stand for 2 days. Neutralisation of the alkali as also the separation of the protein were greatly facilitated by the organic acids and carbon dioxide resulting from the fermentation which accompanied the treatment. The details of the related operations as also the drying of the residual solid and supernatant liquid have been worked out.

5. The nitrogen balances at different stages during the precipitation of the protein and the preparation of the manure have been determined. Non-protein nitrogen, equivalent to 16 per cent. of the nitrogen present in the original cake, is lost during the fermentation preceding the separation of the protein.

6. The conditions for the preparation of water-paints and oil-bound water-paints containing vegetable casein as the binder have been standardised. A number of trials carried out with the products show that they possess excellent covering and adhesive properties, can withstand weathering and are quite washable.

7. Laboratory tests, as also field trials, have shown that the vegetable casein makes a good spreader-adhesive for insecticidal sprays.

8. The possibilities of using vegetable casein in the plastic industry are indicated.

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PETROL-WATER EMULSIONS.

PART II.—REPRODUCIBILITY AND VISCOSITY.

By B. N. Narayanaswamy and H. E. Watson.

In a previous communication (*this Journal*, 1930, **13A,** 21) an account was given of some of the properties of petrol-water emulsions made in a colloid mill with soap solutions as stabilisers. It was pointed out that one of the main difficulties in measurements of this type was the fact that emulsions prepared under apparently identical conditions might differ widely in their properties, a fact well known to workers in this field. While making additional observations on the variation of viscosity with time similar to those described in Part I it was observed in several cases that freshly prepared emulsions gave the most irregular results. A possible explanation was the inclusion of air by the emulsion and this was confirmed experimentally. Shortly afterwards Sibree (*Trans. Faraday Soc.*, 1931, **27,** 168) published similar observations for paraffin emulsions. By excluding air as far as possible and making the process of emulsification continuous, much more consistent values could be obtained. Emulsions so prepared still showed slow changes in viscosity and these have been examined in conjunction with the stability and particle size.

EXPERIMENTAL.

As hydrocarbon mixtures of different densities are known to give different results when emulsified, most of the experiments to be described were made with a fraction of Burmese petrol boiling between 100 and 150° and of density 0·7623 at 25°. In a few drop-number measurements a lower-boiling fraction was employed.

Sodium oleate used as a stabiliser was the purest obtainable. Ammonium oleate was made by passing dry ammonia into a petroleum ether solution of redistilled oleic acid; the white precipitate was washed with petroleum ether and preserved in a desiccator containing dry ammonia. Triethyl-ammonium oleate was prepared by mixing equivalent quantities of oleic acid and triethylamine in aqueous solution.

The emulsions were made in a Premier colloid mill modified as shown in Fig. 1 so as to give continuous circulation of the fluid and to prevent air being drawn into the gap between the rotor R and the stationary portion S. Using 500 c.c. of liquid and allowing it to circulate for about 5 minutes, equivalent to 20 passages through the mill, it was found that the resulting emulsions, when of the same composition and type, had very similar properties. This applied to emulsions made

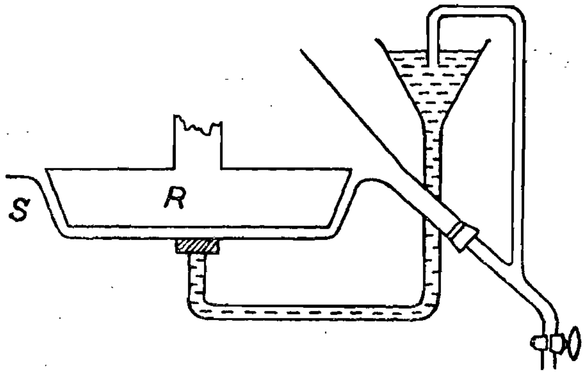

Fig. 1.

directly from the original constituents and to those made by adding one constituent to a previously prepared emulsion of different composition, the final products being indistinguishable.

The type of an emulsion was determined by the drop dilution method and the composition by adding hydrochloric acid to 25 c.c. contained in a burette and reading the volume of the petrol which separated. All percentage compositions given are in terms of volume.

Viscosities were measured at 25° in one of three Ostwald viscometers which were standardised at 20° with a glycerin-water mixture having a density 1·143 and viscosity 0·0794 c.g.s. units at that temperature, the times of flow being 390·4, 66·6 and 50·1 seconds. Objections have been raised to the use of this type of viscometer on the ground that passage through a capillary tends to break an emulsion. No error arising from this cause could be detected in the present experiments, successive readings giving identical values except for a few freshly prepared emulsions the viscosity of which was changing rapidly. Concordant results were also obtained for the same emulsion in different viscometers.

The effect of air.—When preparing emulsions with the colloid mill in its original form which necessitates the intermittent addition of the mixture, air is apt to be sucked in from time to time and this becomes dispersed in fine bubbles throughout the emulsion. The same result is obtained when emulsions are made by shaking in a bottle. It was found that the density of such emulsions was always less than the calculated value and that it increased rapidly at first and more slowly afterwards until the theoretical figure was reached. The initial drop in viscosity was also rapid, but this quantity continued to fall after the density had reached a constant value.

Emulsions from which air had been excluded as far as possible had also a slightly lower density than the calculated value indicating that they contained some air, but the variation of viscosity with time was far less marked.

Some typical figures are shown in Table I, the time t being in hours.

TABLE I.

Density and Viscosity of Emulsions. 1 per cent. Sodium oleate.

(*a*) 48 per cent. P. in W. air.			(*b*) 42 per cent. P. in W. air.			(*c*) 58 per cent. P. in W. no air.			(*d*) 38 per cent. P. in W. no air.		
t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$	t	d	$\eta \times 10^4$
0	0·8749	824	0	0·8870	404	0	0·8570	1632	0	0·9062	318
0·5	0·8798	751	2	0·8921	386	5	0·8584	1632	5	0·9077	314
1	0·8832	711	3	0·8942	376	24	0·8600	1632	24	0·9089	306
44	0·8845	645	4	0·8963	370				27	0·9096	296
116	0·8854	642	24	0·8989	365				48	0·9097	289
140	0·8856	642									
144	do.	641									
164	0·8859	618									
260	do.	608									
284	do.	560									
308	do.	563									
332	do.	517									

It will be observed that in the case of emulsions (*a*) and (*b*) containing air, the rise in density was 11–12 units in the third place corresponding with the presence of 1·2—1·3 per cent. of air by volume. For (*c*) and (*d*) equilibrium was not attained, but taking into account the density values calculated from the composition, the initial quantity of air was about 0·5 and 0·2 per cent. respectively and with this amount the viscosity changes were far less, emulsion (*c*) which was very viscous exhibiting a constant viscosity for 24 hours. If the viscosity values for (*a*) are plotted against time it will be seen that the initial fall is very rapid, subsequently up to about 250 hours the rate of change is slow but it then increases. The first stage is probably due to elimination of the larger bubbles of air, the second is a normal change exhibited by all but the most stable emulsions and the third corresponds with incipient breaking of the emulsion. Similar changes have been observed with many emulsions an interesting case being that of a 44 per cent. petrol in 1 per cent. sodium oleate emulsion the viscosity of which fell slowly from 0·0389 to 0·0346 in 12 days and then dropped to 0·0126 the next day and to 0·0092 two days later. In this case the emulsion showed signs of separation after two days and was gently shaken daily to render it homogeneous.

The part played by air in emulsions is important especially when proteins are used as stabilisers (*cf.* Clayton, *Proc. Chem. Eng. Group*, 1932, **14,** 158) but the above-mentioned experiments indicate that by reducing the quantity of air as far as practicable, emulsions showing small initial viscosity changes can be prepared.

To test the reproducibility of such emulsions four mixtures of petrol and 1 per cent. sodium oleate solution were prepared with the proportion of petrol varying from 28 to 58 per cent. Each was divided into two portions which were emulsified separately until the viscosity became constant. The viscosities of the duplicate emulsions corrected for slight changes in composition during emulsification and measured at equal times after the end of this operation were found to be identical within the limit of experimental error the maximum difference being 0·7 per cent.

Drop-numbers.—Drop-numbers for petrol in several soap solutions were given in Part I. Additional measurements have now been made for the stabilisers used in the present experiments and two petrol fractions boiling at 60–100° and 100–150° respectively. The temperature was 23° and the aqueous solution was allowed to drop into the petrol whereas the reverse procedure was adopted previously. The actual drop-numbers were consequently different, but on multiplying by the arbitrary factor 4·5 they yielded results of the same as before as may be seen from Table II.

TABLE II.

Drop-numbers of 1 per cent. Stabiliser Solutions in Petrol.

Stabiliser.	60–100°.	100–150°.	Former value.
Sodium oleate ..	262	257	226
Triethylammonium oleate ..	117	112	..
Ammonium oleate ..	68	68	70
Water ..	..	34	38

Stability and Viscosity.—Numerous emulsions have been prepared and their stability and viscosity examined. In all cases emulsification was conducted until the viscosity became constant and air was excluded as far as possible. Some emulsions were prepared directly, others by diluting an emulsion with one of the components and re-emulsifying. The latter process was more convenient when it was desired to prevent a change of type. When the type was the same, emulsions prepared by both methods had identical properties. Table III gives the time which elapsed before initial separation was visible. The disperse phase (petrol or water) is noted in column 3. The letter M denotes emulsions of mixed type which will be referred to later.

Stability and Composition of Emulsions.

Stabiliser.	Petrol per cent.	Disperse phase.	Time for separation
1 % sodium oleate ..	90	W	< 1 m.
	80	W	4 ms.
	73·3	P	...
	52	P	1 day
	50	P	1 day
	44	P	2 days
	40	P	2 days
	20	P	4 days
	10	P	10 days
	8	P	10 days
1 % triethylammonium oleate	90	..	< 1 m.
	76·5	P	2 ms.
	51	P	1 day
	46	P	1 day
	32·8	P	1 day
	24·4	P	1½ days
1 % ammonium oleate	80	..	< 1 m.
	74	P	30 ms.
	60	P	40 ms.
	52	P	1 hr.
	38	P	4·5 hrs.
	36·8	P	5 hrs.
	8	P	5 hrs.
5 % triethylammonium oleate	90	..	< 1 m.
	80	W	3 ms.
	68·6	P	1 day
	61·2	P	2 days
5 % ammonium oleate	62·6	W	10 ms.
	53·6	W	30 ms.
	41·2	W	10 days
	40	W	Stable
	35·6	W	do.
	31·2	W	do.
	27	W	do.
	15	W	do.
	31·2	P	Stable
	29·6	P	do.
	23·6	P	do.
	20·0	P	do.
	12	P	do.
	8·4	P	do.
	48·8	M	Stable
	36	M	do.
	32	M	do.
	30·2	M	do.

The results in general resemble those given in Part I but they are much more uniform owing to the improved method of preparation. The former figures were mostly for higher concentrations of stabiliser than were used in the present experiments and so a close comparison is not possible. A striking difference, however, is to be found in the results for one per cent. sodium oleate solutions with less than 40% of petrol. These were previously obtained by direct mixing and were very unstable; the present series was obtained by dilution and also by direct mixing, and the emulsions were stable for several days. The reason may be the difference in the petrol used or effect of air since it has been pointed out by Clayton (*loc. cit.*), a gas may have a very marked effect upon the stability. As before, water in petrol emulsions could be obtained with sodium oleate when the proportion of petrol was large and the same effect was observed with triethylammonium oleate but only with 5 per cent. solutions and in all cases these emulsions were very unstable. With 5 per cent ammonium oleate the proportion of petrol could be reduced to 15 per cent. without producing a change in type, and these emulsions were very stable. This may indicate that the strength of the base is a more important factor than the drop-number in determining the type and stability. In this case concentration has a marked influence, water in petrol emulsions not being obtained with 1 per cent. of stabiliser. With sodium oleate on the other hand a 5 per cent. solution gave results differing very slightly from those with the smaller quantity.

The viscosities of the more stable emulsions referred to in the Table III as well as those of several others were measured and the results plotted on a logarithmic scale are shown in figs. 2 and 3. It will be noticed that the experimental points lie much closer to the curves than those given in Part I. The curves for 1 per cent. sodium oleate and triethylammonium oleate are nearly straight for proportions of petrol below 45 per cent. but it is remarkable that emulsions made with the latter emulsifier have approximately 6 times the viscosity of those made with the former. With ammonium oleate the curvature is in the opposite direction and much more pronounced, while at higher petrol concentrations there is an abrupt bend indicating perhaps an incipient change in type. With these stabilisers no water in petrol emulsions sufficiently stable for measurement could be obtained. Fig. 3 shows the results for 5 per cent. ammonium oleate. In this case stable water in petrol emulsions were obtained over a wide range, two of which with 27 and 15 per cent. of petrol were semi-solid so that their viscosity could not be measured. These were made by emulsifying a mixture of 55 parts of petrol and 45 of water, adding water to the product and again emulsifying. This process was repeated until the emulsion became too viscous to put through the mill. It is remarkable that although the disperse phase was added there was no change in

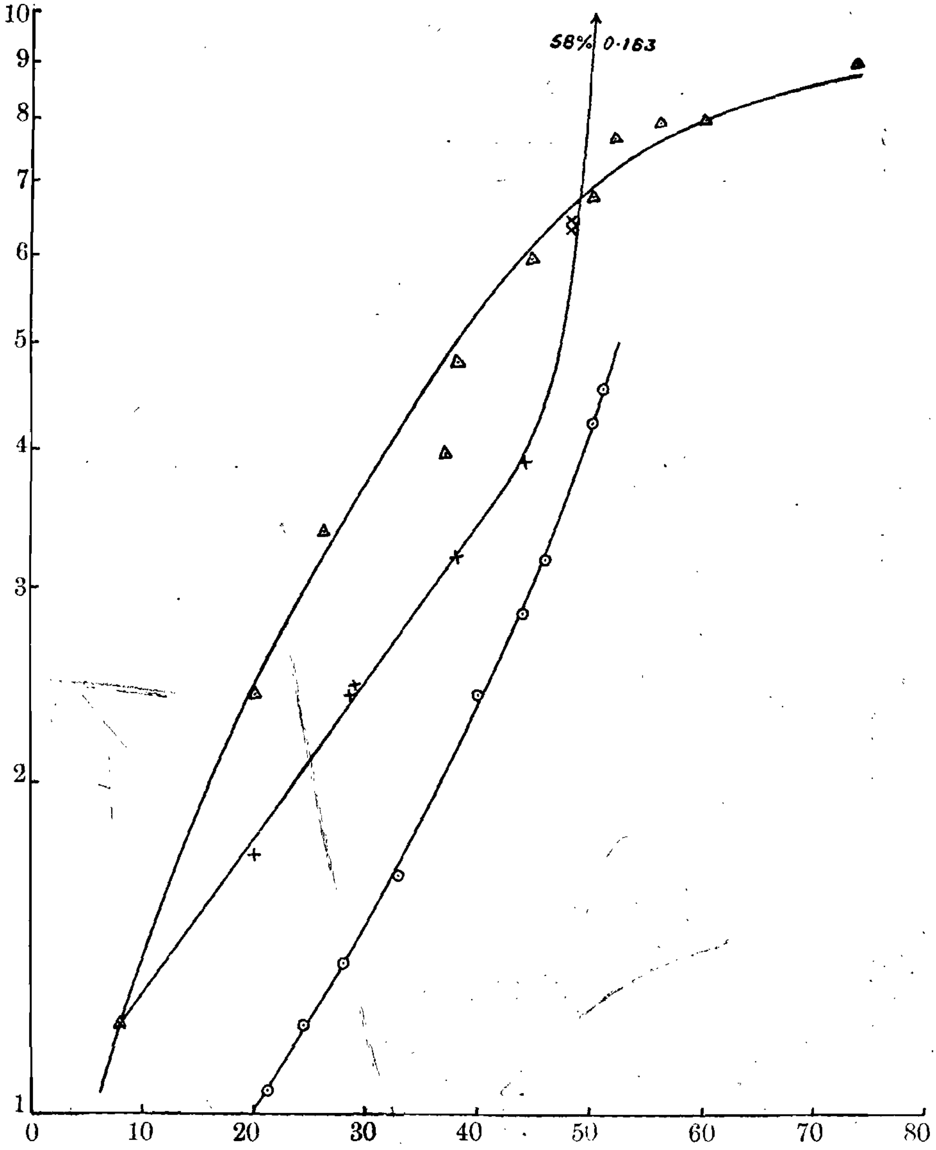

Fig. 2.

⊙ 1% Triethyl-oleate.
× ,, Sodium-oleate.
△ ,, Ammonium-oleate.

type. Petrol in water emulsions containing 8·2 to 31·2 per cent. of petrol were prepared in a similar way by adding successive quantities of petrol to the 8·4 per cent. emulsion and again emulsifying. In this case when the proportion of petrol exceeded 31 per cent. a change in

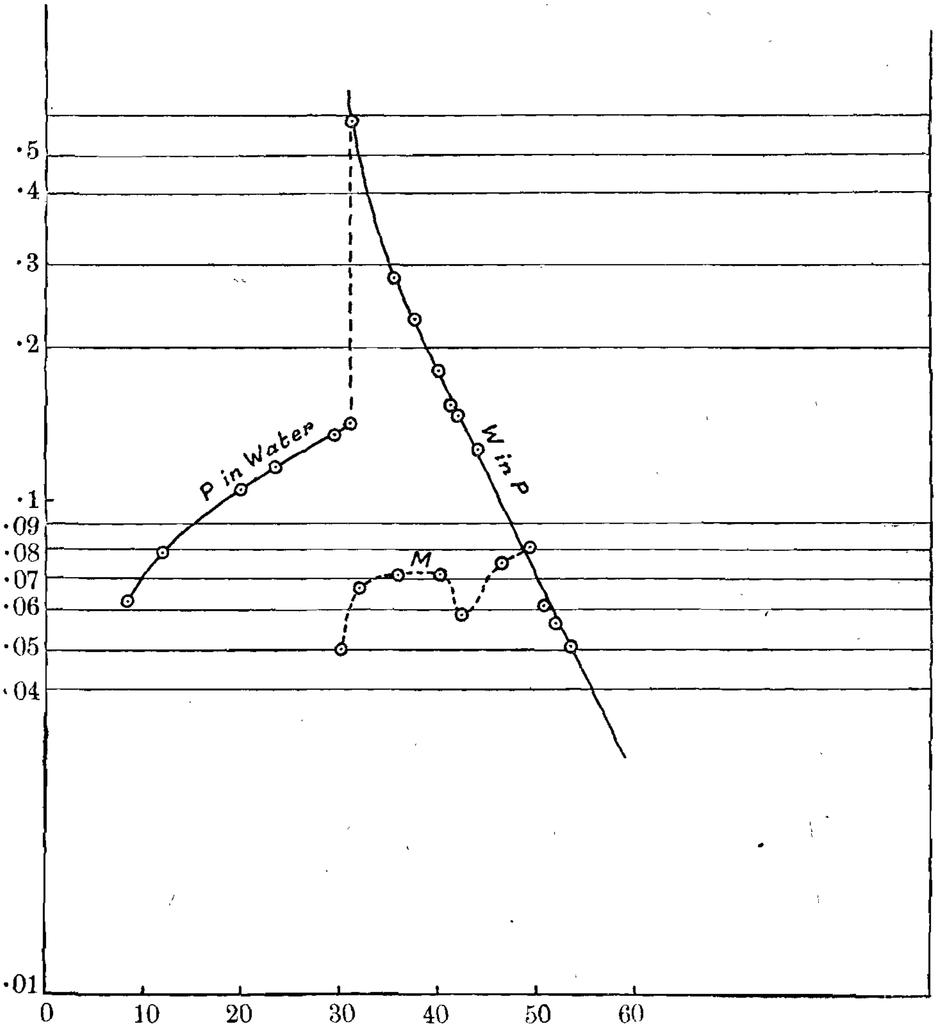

Fig. 3.

5% Ammonium-oleate.

type occurred yielding a product with very low viscosity. Examination under the microscope and the behaviour on addition of a drop of one of the constituents indicated that this emulsion was of the mixed type (*cf.* Clayton, *loc. cit.*). On addition of more petrol, other mixed emulsions were obtained the viscosity of which did not change appreciably with composition. If the proportion of petrol exceeded 50 per cent. a change to the water in petrol type took place. Mixed emulsions with similar viscosity could also be obtained by direct emulsification of mixtures containing between 32 and 45 per cent. of petrol although in some cases the product was of the water in petrol type.

Particle size.—The 5 per cent. ammonium oleate emulsions were xamined under the microscope and the approximate size of the particles etermined. The results are shown in Table IV.

TABLE IV.

Petrol per cent.	Disperse phase.	Average size, μ.
52	W	4
40	W	8
37·6	W	20
32	W	80
27	W	200
15	W	do.
31	P	90
40·2	M	60–200
46·4	M	do.

In the case of the water in petrol emulsions the particle size ecreased in a marked manner as the amount of petrol increased, that s to say, as the viscosity decreased. It is difficult to say whether this elation is accidental owing to the fact that water is more easily disersed in solutions of low viscosity or whether there is a definite endency for the particle size to depend on the composition of the mulsion. In view of the fact that emulsification was continued in all ases until the viscosity became constant and that although the petrol n water and mixed emulsions had a low viscosity, the particle size was rge, it would appear that the second explanation is the more probable. upport is lent to this view by the fairly homogeneous nature of the ater in petrol emulsions. The emulsions of mixed type contained articles of very different sizes although not many were small. It is omewhat remarkable that these indefinite mixtures all had a viscosity of he same order.

The relation between composition and viscosity.—As already menioned the composition-viscosity curves shown in figs. 2 and 3 tend o be of a linear type within certain ranges of composition, showing that he relation is a logarithmic one.

To a first approximation the following equations hold good :—

Stabiliser.	Equation.	Observed η_0.	Range of ϕ.
per cent. sodium oleate	$\text{Log}\ (\eta/0{\cdot}0093)=1{\cdot}42\phi$	0.0107	0·08–0·45
per cent. triethylammonium oleate	$\text{Log}\ (\eta/0.046)=1{\cdot}94\phi$	0·0113	0·13–0·45
per cent. ammonium oleate P in W.	$\text{Log}\ (\eta/0{\cdot}061)=1{\cdot}17\phi$	0·0213	0·20–0·30
per cent. ammonium W in P.	$\text{Log}\ (\eta/0{\cdot}00051)=4{\cdot}26\phi$		0·45–0·65

vhere ϕ is the ratio of the volume of the disperse phase to that of he continuous phase. The curve for 1 per cent. ammonium oleate could not be represented by an equation of this type. These equations do not correspond exactly with that of Arrhenius $\log (\eta/\eta_0) = K\phi$ where η_0 is the viscosity of the continuous phase. The values of this quantity are given above and although the divisor of η in the case of sodium oleate is not far from η_0, for the other stabilisers the difference is much larger. It is remarkable that the curves of both 1 and 5 per cent. ammonium oleate petrol in water emulsions are concave towards the axis of X, whereas in the other cases there is a sharp upward trend as the limit is approached at which a change in type takes place.

It is evident therefore that although the relative volume of the phases is of importance in determining the viscosity, several other factors must be taken into consideration and before definite conclusions can be reached it will be necessary to make an extensive study of particle size, adsorptions of the continuous phase and the effect of stabilisers with different degrees of dissociation, to mention only the main items which affect the problem.

SUMMARY.

1. It has been found that many of the irregularities previously observed in the physical properties of apparently identical petrol-water emulsions were due to the presence of air. By excluding air and continuing the emulsification until the viscosity became constant, reproducible values have been obtained.

2. Emulsions have been prepared with sodium, triethylammonium and ammonium oleates as stabilisers and their viscosities measured. The first two stabilisers yield mainly petrol-in-water emulsions, the water-in-petrol type obtained with high proportions of petrol being very unstable. 5 per cent. ammonium oleate gives stable emulsions of both types and also a series of mixed type characterised by large particle size and low viscosity.

3. The relation between viscosity and composition is in most cases of logarithmic type over a considerable proportion of the stable range, but the equation connecting the two quantities is not that of Arrhenius.

In conclusion, we express our best thanks to Mr. S. K. Jatkar for his valuable assistance throughout the course of this work.

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PREPARATION OF SUGAR SYRUP FROM CASHEW APPLE (*Anacardium occidentale,* LINN).

By M. Srinivasan.

The cashew is a hardy tree that thrives well in many parts of India, especially on the west coast, where it is largely grown for its valuable nut. After the removal of the nut, there remains the fleshy and succulent portion, the cashew apple, more popularly known as the cashew fruit. This apple is soft and sweet and possesses a strong aroma. It has, besides, an astringent principle which curtails its use as an edible fruit. The juice of the apple can be fermented either to yield a beverage, or to produce vinegar (Rama Iyer, *Scientific Reports*, *Agricultural Research Institute*, Pusa, 1930, 55). The production of the fruit is, however, far in excess of the demand, and being readily perishable, the available supply is largely wasted.

In a previous communication (Subrahmanyan, Report to the Director of Industries, Madras, 1932—unpublished) it was pointed out that though alcohol could be obtained from cashew apple by fermentation, the cost of its preparation does not warrant large scale production, and hence the juice could be more usefully converted into syrup. The present paper relates to a systematic enquiry on the utilisation of cashew apple for the preparation of sugar syrup.

EXPERIMENTAL.

Materials.—Several consignments of cashew apple were obtained through the courtesy of the Honorary Secretary, District Advancement Association, South Kanara, to whom the author's thanks are due. When received in Bangalore, however, these fruits were found to have mostly decayed. The apples were, therefore, bought from the local Palace Orchards. They were brought to the laboratory immediately after plucking and used for the experiments.

Examination of the Fruit.—Total solids were determined according to Hughes and Maunsell (*Analyst*. 1934, **59**, 231). The apples were cut into thin slices and a known weight (1 to 2 g.) weighed from a squat type of weighing bottle into a tared platinum dish (100 c.c.). Hot distilled water was added to distribute the sample evenly over the bottom of the dish, and placed on a water-bath till almost dry, the last traces of water being removed by heating in a vacuum oven at 100° till the weight was constant. To find out the extreme variations, two samples, (1) unripe (pale-yellow in colour and hard to feel), and (2) fully ripe (red and soft) were analysed. The former yielded

48 per cent. and the latter 14·9 per cent. of total solids on the fresh weight of the apple.

Sugars.—About 10 g. of sample was refluxed with 200 c.c. of 95 per cent. alcohol for about one hour. The alcoholic extract was filtered and the residue washed twice with alcohol. From the combined filtrates, alcohol was distilled off at a low temperature (50°). The residue left in the flask was dissolved in hot water, transferred to a 500 c.c. measuring flask, and made to volume. 25 c.c. of the solution were clarified with 2 to 3 c.c. of normal lead acetate solution, made upto 100 c.c. and filtered. 50 c.c. of the filtrate were deleaded with sodium phosphate, made upto 100 c.c., and again filtered. Sugar was estimated according to Bertrand in 20 c.c. portions of the filtrate.

Another aliquot was inverted, and the resulting sugars estimated as before, there being practically no difference in value before and after inversion (Table I).

TABLE I.

Sugar content of cashew apple.

Condition of Fruit	Reducing sugar per cent. (as invert sugar on fresh weight of the apple)	
	Before inversion	*After inversion*
Unripe	4·1	4·3
Half ripe	5·3	5·3
Ripe	7·0	7·0
Fully ripe	7·2	7·2

The above results show that the sugar content of the cashew apple depends on the extent of its ripeness. The unripe apple has the minimum sugar content, while the ripe one has the maximum, others between these stages having corresponding intermediate values.

At none of the stages of ripeness was there any evidence of cane sugar being present. The origin of reducing sugars in the apple would, therefore, appear to be a highly interesting line of enquiry.

Experiments with the juice.—The juice obtained by pressing the minced cashew apple through cloth (*vide infra*) was turbid. On examination under the microscope, it was found to be teeming with micro-organisms. It was further characterised by powerful reducing action, which was greatly diminished, however, by ærating the warm juice (50°) for half an hour. This behaviour suggests the presence of ascorbic acid—vitamin C (Watt, *Commercial Products of India*, p. 65) in the juice.

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Analysis of the juice.—The following is a proximate analysis of the juice, the analytical methods employed being those recommended by A.O.A.C. (1931) for fruits and fruit products :—pH, 4·2 to 4·6; titratable acidity, 6·7 c.c. (N acid); density, 1040; total solids, 10·6 per cent.; and ash, 0·36 per cent.—all on volume basis.

On being moistened with water, the ash was found to be alkaline to litmus. It also yielded a positive test for phosphorus.

The sugars were estimated by reduction (Bertrand) and polarization methods, both before and after inversion.

TABLE II.

Sugar (as invert sugar) per 100 c.c. of the juice.

Sample	Before clarification g.	After clarification		$[\alpha]_D^{26}$
		Before inversion g.	After inversion g.	
1	9·6	9·2	9·7	−16·0
2	9·5	9·1	9·9	,,
3	10·0	9·5	9·9	,,

The small increase in the total sugar value after inversion indicates that there is very little cane sugar even in the juice. The reducing sugars correspond on an average to 95 per cent. of the total solids, or 98 per cent. of the organic solutes present in the juice.

Nature of sugars.—The specific rotation $[\alpha]_D^{26} = -16°$ of the cashew juice after clarification indicates the presence of invert sugar, $[\alpha]_D^{20} = -20°$. In further confirmation of the presence of invert sugar in the medium, the clarified juice gave positive colour reactions both for glucose and fructose, while the osazone prepared therefrom was purely that of glucose (equally of fructose).

Other constituents of the juice.—As indicated in a previous communication (Subrahmanyan, *loc. cit.*), the juice contained considerable quantities of tannins, organic acids and an astringent principle. It had also the penetrating odour of the whole apple, and was pale yellow in colour. The odour was removed by vigorous boiling of the juice. The colour was traced to the pigments extracted from the outer skin of the apple during mincing and pressing. The extracted pigments were of the nature of anthocyanins, as evidenced by the characteristic pink colour the juice developed on the addition of concentrated hydrochloric acid.

PREPARATION OF SYRUP.

The methods employed to prepare sugar syrup from cashew apple were those usually adopted in obtaining raw sugars from cane or beet. Such methods involved (1) extraction of juice from the apple, (2) defecation and clarification of the juice by heat, chemicals or filtration, (3) concentration of the clarified juice by fire, steam or vacuum evaporation, and (4) purification (curing) of the resulting product.

Extraction of juice from cashew apple.—Working with small numbers of the apples, it was found that a very simple but efficient method of expressing the juice was to mince the fruits and squeeze the resulting mass through folds of cloth. An aluminium mincer was used for the purpose. This method of extraction gave fairly uniform yields of juice as shown by Table III. Use of iron-ware was found undesirable, since it yielded a bluish-black extract, the colour being due to the reaction between the metal and the acids and tannins of the juice.

TABLE III.

Yield of juice from cashew apple.

Condition of the apple	Number	Yield of juice c.c.	Yield of juice per apple c.c.
Fully ripe, weighing 75·8 g. ..	1	55	55
Unripe, weighing 255 g. ..	7	90	13
Collection, ripe (major portion), half-ripe and unripe ..	100	2,400	24
,,	1,150	27,200	24
,,	1,300	29,000	22

It may be seen from the above that when a representative collection (including fruits at various stages of ripeness) is crushed, the average yield of juice may be reckoned at 20 to 25 c.c. per apple.

The state of ripeness of the cashew apple not only regulates the yield of juice, but so controls the efficiency of pressing. Thus, in case of the fully ripe, soft apple, it was found that squeezing the minced mass through cloth extracted 85 per cent. of the total sugars, while in case of the hard, unripe one, only 70 per cent. was expressed, demonstrating the need for greater pressure in the latter case. Leaching with water, however, removed most of the residual sugars from both the pressed cakes. On a commercial scale, a more efficient pressing could be carried out with the aid of machinery; but it is very necessary, for reasons already mentioned, that the juice should, under no circumstance, come directly into contact with iron. Nickel-plated iron presses, or wooden ones could be used.

Preservation of juice.—Since the cloth-filtered juice, abounding in microflora, began to ferment rapidly, it was necessary to sterilise it, either by treating with chemicals (sulphur-dioxide), or by heating in steam under pressure. In following the first method, about 35 litres of the filtered juice, contained in a 50-litre carboy, were treated with sulphur-dioxide, the carboy plugged with cotton, and preserved in ice room (−2°). The second method consisted in sterilising a similar carboy, containing about 30 litres of the juice, directly in an autoclave for 10 mins. at 15 lbs. After sterilisation, the carboy was allowed to cool in the autoclave. After cooling there was a deposit of some debris, while the supernatant was clear but orange-red in colour, due to partial caramelisation of sugars. Along with the carboy for sterilisation in the autoclave, were kept each time six conical flasks (500 c.c.), containing cashew juice, with which preliminary trials were conducted.

The juice, sterilised and preserved by the above methods, formed the material for the preparation of sugar syrup.

Defecation.—Preliminary analysis having shown that the cashew juice contains mainly invert sugar, the usual methods of defecation of cane juice could not be adopted. Great care was necessary in adopting lime as a defecator, since even a slight excess of it resulted in caramelisation of the sugars present. Though calcium carbonate has been often used in place of lime for defecating sugar juices, it was found in the present instance, that addition of calcium carbonate even in quantities far in excess of the amount needed to neutralise the juice, did not completely remove the acids, thus resulting in insufficient precipitation of albuminoids and tannins. While the use of lime was thus indispensable, still an excess of it had to be carefully avoided, to prevent caramelisation of sugars and redissolution of coagulated impurities.

Behaviour of cashew juice on addition of lime.—On adding increasing quantities of milk of lime to cashew juice and shaking, the juice, fresh or steam sterilised, turned reddish-black. Addition of 20 per cent. of the total quantity of lime calculated to bring the medium to neutrality, brought about this initial colour change. Addition of a greater portion of the balance darkened this colour, and imparted a turbidity to the juice. When all the lime was added, the turbidity culminated in a sudden coagulation. The separated mass dispersed evenly through the medium, imparted to it a dull grey appearance. On now stopping both the addition of lime and shaking, a clear supernatant tinged slightly greenish yellow, was formed. This supernatant, neutral to litmus, was found to filter easily through filter paper, and even better, through cloth (by gravity), giving a clear filtrate. When lime was in excess, the filtrate was coloured yellow.

The correct amount of lime would have been added to the cashew juice, only when the coagulum in the juice precipitates down completely, giving a pale yellow, easily filterable supernatant, almost immediately after shaking is discontinued. The filtrate will now be found neutral. The coagulum on the filter, containing a mixture of tannins, albuminoids and colouring matter, will be slimy and chocolate coloured.

Thus it should be possible, with some experience, to accurately neutralise the acidity in cashew juice, and thereby remove tannins and albuminoids by lime treatment, even without the adventitious aid of special indicators, the necessary colour change being shown by the pigments present in the juice.

The quantity of lime required to neutralise the juice was found to be about 0·2 g. per 100 c.c. of juice. Lime was used in the form of milk, and the reaction was conducted in the cold.

Clarification.—The filtrate from the above, sweeter than before due to removal of acids, tannins and astringent principle, but containing more calcium salts in solution, had now to be clarified. This had to be carried out before beginning to concentrate the juice; otherwise, the calcium salts would be precipitated and dispersed evenly through the syrup rendering it turbid, and difficult to be decalcified by filtration, or otherwise. Further, such a syrup would acquire a bitter taste which is ascribed to the calcium ion. According to Paine, Keane and McCalip (*J. Ind. Eng. Chem.*, 1928, **20**, 262), calcium salts are more detrimental to metabolism than generally recognised. So, most of the calcium salts were removed from the defecated juice by using sulphur-dioxide, carbon-dioxide or phosphoric acid. The removal of calcium from solution as insoluble salts of these three acids was almost complete. A greater portion of the residual calcium was removed from the final syrup by filtration (see *infra*).

Concentration.—Concentration of the defecated and clarified cashew juice was conducted in enamelled iron vessels. The vessels containing the juice were heated in one instance over a ring burner, and in another over a water-bath, the contents of the vessel in either case being kept well stirred during concentration. The burner took about 5 hours, and the water-bath 8 hours to concentrate 20 litres of the juice to the same syrupy consistency (70–80 per cent. sugars). From the intensity of colour, it appeared that caramelisation had occurred to about the same extent in both the cases, thereby showing that water-bath offered no special advantage over the quicker direct fire, as a means of concentration.

Extent of concentration.—The gravity, as determined by the hydrometer, is a useful measure of the sugar content of the defecated and clarified juice at any moment during the process of concentration. A more practical, though less accurate, method is to judge the sugar concentration from the consistency of the syrup. This was the guiding factor in preparing the syrup from cashew juice. Concentration of the juice was continued upto a point when the resulting hot viscous syrup, taken at the end of a glass rod, poured slowly at first, then formed a thread as it cooled, and finally broke off from the edge—the sort of test that confectioners adopt in the preparation of fruit jellies. Such a syrup was found to assume a semi-solid state on cooling, corresponding to a sugar strength of about 80 per cent.

Filtration of the syrup.—With the increase in the concentration of the juice, there was correspondingly greater amount of turbidity, due to separation of the residual calcium salts. This sediment in the final concentrated syrup was filtered off with the aid of a water heated Hirsch funnel attached to the top of a Witt's apparatus. The bottom of the Hirsch funnel was covered with a filter paper. The wide bell jar portion of the Witt's apparatus contained the receiver (wide-mouthed bottles for large quantities and sample tubes for smaller quantities of the syrup) in which the syrups were to be finally stored. The Witt's apparatus was connected to an ordinary water pump, while the funnel was kept hot by heating the water in the jacket. The turbid syrup was poured into the funnel, and under the influence of suction and heat, it filtered through easily. A further modification of the method contemplated is to use in place of the filter paper covering the Hirsch funnel, a bed composed of alternate layers of paper pulp, and some other porous materials like kieselguhr or Supercell, as has been recommended for filtering fruit juices and plant extracts (Hall and Baier, *J. Ind. Eng. Chem. Anal. Edn.*, 1934, **6**, 208).

Properties of the syrup.—The syrup obtained according to the above procedure was in every instance cherry red in colour. A sample, obtained by boiling down the original juice as such to a syrupy consistency without defecation, was found to have a mixed taste of jaggery on the one hand, and acids and tannins on the other. Another sample, defecated but containing the calcium salts precipitated in the final stages, had the same colour as the first sample, but less turbid and tasted better. Removal of calcium salts and other suspended impurities from the latter sample resulted in a clear syrup though equally coloured.

The colour in all these cases was mostly due to the presence of caramel. When the starting material for the preparation of syrup was the sulphur-dioxide treated juice, the resulting syrup had a bright colour, though it had the unpleasant residual taste of the preservative. On the other hand, using steam sterilised juice, the caramel originally present in it was concentrated during heating, yielding a dark coloured syrup resembling treacle.

Curing.—A few experiments were tried to refine the coloured syrups. The usual method of dissolving a small quantity of raw sugars in water, and agitating the resulting solution with various decolourising carbons did not result in any improvement. The following decolourising carbons were tried:—Norit, bone or blood charcoal, paddy husk and cocoanut shell charcoals. On passing the mixture through a small basket centrifuge, a clear centrifugate was obtained, but the original dark colour of the syrup persisted. Preliminary treatment with porous materials like kaolin, kieselguhr or pumice did not also improve the colour. Next, the caramelised juice was concentrated to about 60 per cent. of its original volume, and then defecated in the hope that the defecation scum would carry down with it at least a part of the caramel. The results were again not satisfactory. Defecation by normal lead acetate, followed by the removal of lead by hydrogen sulphide, did not also result in any advantage.

Concentration of the juice in vacuum, and other methods of preventing caramelisation of invert sugar present in the cashew juice, are now being tried. It is hoped that the results of these trials would form the subject of a later communication.

Uses.—The conversion of cashew apple juice into a syrup, containing eight times more invert sugar than the original juice, is a useful method of conserving the sugars in this apple, now running to waste. Once the juice has been converted to a syrup, this may be sold as such like the golden syrup, the melon and maple syrups, or used as raw material for the production of alcohol by fermentation. It may serve also as a bloomer to many syrups. Sold as an edible syrup, the quality might be improved by lending it a mild sub-acid taste. Syrups retaining the original aroma might also be prepared to cater to the tastes of people who like the cashew apple flavour.

The fact that cashew syrup contains mostly invert sugar enhances its value considerably. Invert sugar is in such great demand, being much used in the manufacture of artificial honey. Honey itself contains invert sugar to the extent of 65 to 80 per cent.

The water-holding capacity of invert sugar to the extent of 14 per cent., leaving it always syrupy, makes it indispensable for confectioners and bakers, while its easy assimilability, being a pre-digested sugar, renders it eminently suitable for inclusion in infant and invalid foods. Moreover, it is 25 per cent. sweeter than cane sugar (Biester, Wood and

Wahlin, *Amer. J. Physiol.*, 1925, **73,** 387). These remarks apply equally to cashew syrup, containing as it does mostly invert sugar.

Large quantities of invert sugar are required for use in confectionary. Since the total consumption of confectionary in India (including imports) amounts to several hundred tons per annum, there would appear to be prospects of a big demand for cashew syrup, if it could be produced in sufficiently large quantities.

Furthermore, special attention must be drawn to the use of invert sugar in tobacco industry as a "casing" for some cigarette tobaccos to hold the short tobacco with the long, and to keep moisture in the tobacco at the same time. Cashew syrups might thus be useful in this industry, the advancement of which is now being sponsored by the Imperial Council of Agricultural Research.

Cashew syrup may also serve as a useful source for levulose production. Levulose, it might be added, is of great medicinal value, because of the remarkable tolerance exhibited by diabetic patients, for which purpose it is now manufactured from Jerusalem artichoke.

If a biological assay confirms the finding that cashew juice contains vitamin C, the syrup may be so prepared as to include this vitamin.

SUMMARY.

1. By analytical methods it has been found that cashew apple contains invert sugar, about 7 per cent. on the fresh weight of the apple.

2. Each cashew apple yields on an average 20 to 25 c.c. of juice, having 10·4 per cent. of total solids. Sugars alone account for 94 per cent. of the total solids in the juice. The remaining part is made up of acids, tannins, an astringent principle and pigments. Preliminary observations have also shown that the juice contains vitamin C.

The juice does not keep and ferments very readily, unless sterilised by heat, or treated with preservatives (SO_2) and cold.

3. The riper the fruit, the greater is its yield of juice and larger the sugar content.

4. The usual methods of defecation and clarification of sugar juices have been modified to suit this juice, which contains mostly invert sugar.

5. It has been found that pigments present in the juice facilitate the correct addition of lime, which is further aided by the finding that at neutral pH, there is complete precipitation of albuminoids and tannins, and that the medium allows of easy filtration.

6. The removal of calcium salts appearing during concentration of the juice, even after preliminary precipitation of most of them as carbonate, sulphite or phosphate, is effected by filtration aided by heat and suction.

7. The uses of the resulting syrup are discussed.

In conclusion, the author wishes to thank Professor V. Subrahmanyan for guidance and Mr. B. N. Banerjee for helpful suggestions. He also wishes to acknowledge the grant of a scholarship from the Department of Industries, Madras, which enabled him to carry out this work.

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UTILIZATION OF INDIGENOUS TANNING MATERIALS.

PART I. MANUFACTURE OF TANNIN EXTRACT FROM AVARAM BARK (*CASSIA AURICULATA*, LINN).

By Keshaviah Aswath Narain Rao and Shaha L. Janniah.

Avaram bark, also known as Turwad, Turwar, Avla, Thangadi and Tanner's Cassia, is the most important tan-bark of South India. It is obtained from *Cassia auriculata*, Linn., a bush which grows wild in the South and West of India, covering large areas in the Deccan. It is also found in the dry zone of upper Burma. The right of collecting the bark from Government forests in India has for years been granted on contract, usually put up to auction, by the Forest Department. The bark is, however, much more plentiful outside reserve forests, occurring on most village lands. The method of collection consists in cutting off at the base, branches and twigs which spring from the roots. The coppiced bush sends out a large number of shoots, and a new harvest can be taken after a year.

The use of the bark is more or less confined to Southern India, where in the past, it was the principal material for tanning hides and sheep and goat skins. The amount of bark collected in Madras provides only a part of the local requirements, two-thirds of the total quantity employed being obtained from Mysore and Hyderabad. In Mysore, it is found in abundance in all the Maidan Districts and in the Maidan Taluks of the Malnad. Though information as to the actual quantity of bark collected annually is not easily available on account of collection being done by contractors, the quantity annually disposed of is estimated at 11,000 tons (1914–1915). The income from this tan-bark formed a large percentage of the revenue from minor forest products; an amount of Rs. 2,80,700 was realised in 1914–15 (*Commercial Guide to the Forest Economic Products of Mysore*, 1917, pp. 136–137). The value of the bark can be better realised when it is mentioned that the bark exported from the State during 1927–28 and 1928–29 was respectively 1,68,000 maunds and 2,28,000 maunds, valued at Rs. 10·24 lakhs and Rs. 13·24 lakhs.

The history of the Avaram bark tanning industry underwent a serious change after the year 1915. It was just at this period that the Wattle bark industry in South Africa developed considerably, resulting in large exports of Wattle bark and extract and that, at a very low cost. The effect of this can be realised from the figures of the Indian Official Returns (*Bulletin of the Imperial Institute*, "*Tanning Materials* *of the British Empire,*" 1929, p. 22). While the import of Natal bark was 25,952 cwts. during 1915-16, it was 176,615 cwts. during 1927-28.

The South Indian tanners found, on a comparative basis, that Wattle-tanned hides weighed more than Avaram-tanned ones. Since the South Indian tanned hides are sold by weight, instead of by area, this presented an attractive feature to the tanners. Moreover the weight of Wattle bark required for tanning a quantity of hide was only half that of Avaram bark required; this is due to the high tannin-content of Wattle. Wattle is an astringent catechol tannin, lending itself particularly to sole-leather manufacture ; but it can also be used very successfully for making light leather, and the colour of the leather is much lighter (and much less affected by exposure) than that obtained from many other catechol tannins. It also makes a very good blend with acid-producing tanning materials, such as Myrobalams, yielding a firm and durable leather.

Further, during the war, the enormous demand for Avaram bark, consequent upon the necessity for increased output of the South Indian tanneries, caused many areas to be stripped in such a way that the supply was seriously affected and great anxiety was manifested as to the renewal of regular supplies. The usual price of Avaram was about Rs. 45 per baram of 500 lbs. which jumped during the war to Rs. 100 per baram. The export of Wattle bark to Germany and England having ceased during this period, this bark was forced on the Indian Market. At first, very few tanneries in Bangalore took to it ; but due to various causes, the price steadily dropped from £ 20 to £ 9-10-0 per ton.

The present market rate of Avaram is Rs. 25 a baram. The price obtained for the tanned hides does not permit its use at such a high cost, as the principal tanning agent. The local bark can be used in preference to Wattle only if Avaram is sold at Rs. 15 or less a baram. The matter is more serious now on account of the abolition of import duty on Wattle from April 1930.

In spite of these considerations most tanners still prefer to use Avaram for tanning sheep and goat skins for which it is still the best tanning material. Indeed, the success of the tanning industry in South India is regarded as almost entirely due to the peculiar qualities of Avaram, which is excellent for manufacturing certain types of leather.

Under these circumstances, the question of making available to the tanners, the tannin in Avaram at an economical price has been seriously taken up. The possibility of manufacturing a satisfactory tannin extract in the locality where the bark is available and supplying it to the tanners at Bangalore has been investigated in the first instance.

The advantages of extracts over the raw materials are many. A high percentage of tannins is offered to the tanners in a small bulk and transport charges are lowered considerably; at least 90–95 per cent. of the tannins in the raw material is made available to the tanner; and all the tannins being in a readily soluble form, the period of tanning is considerably reduced. Moreover, the tanner is assured of the supply of a material of uniform quality, instead of a bark each piece of which varies in its tannin-content. The most important condition is that the extract should retain all the good characteristics of the raw material.

EXPERIMENTAL.

This Indian tanning material has been the subject of extensive investigations by Limaye, Mehd and Fraymonth, and Pilgrim. It is also mentioned in the earlier reports on the Indian Leather Trade by Guthrie and Chatterton.

Tannin content.—The tannin-content of Avaram bark varies from 12 to 18 per cent., though samples containing 20 and 23 per cent. have been mentioned (*The Bulletin of the Imperial Institute*, "*Tanning Materials of the British Empire*", 1929). In order to have an idea of the tannin-content of the samples of bark from different parts of the State, a collection of about 2,000 lbs. was made. The analyses carried out on these samples are tabulated below:

TABLE I.

Calculated to 10% moisture.

Sample	Percentages	
	Tans	Non-tans
From Peenya Plantation (Yeswantpur, Bangalore District)	15·0	11·3
From Srinivasapur (Kolar District)	18·0	10·6
Mixed sample (from Bangalore, Kolar and Tumkur Districts)	13·3	17·9
From Local Tannery	12.3	13·6

(All the tannin estimations in this work were done by the Hide Powder method, as prescribed by the I. L. T. A.)

It is seen from the figures given above, that though individual samples may contain tannins from 15 to 18 per cent. and have the ratio of Tans/Non-tans greater than one, the tanners obtain rather poor grades of bark containing only 12 to 13 per cent. tannins, with the ratio, tans/non-tans very often less than one.

The tannin-content depends very much on the age, and the parts of the plant cut. The former has been clearly pointed out by Seshachalam Choudary and Yoganandam ("Studies in Avaram Bark" 1, *Jour. Int. Soc. L.T.C.*, 1928, **12,** 55-58) who found that tannin-content varied from 15·58 per cent. in a shrub one year old to 19·06 per cent. in one of 6 years. They came to the conclusion that it was best to collect the bark from plants five years old. Also, the bark taken from the lower part of the plant is usually richer in tannin than that taken from the upper parts. Limaye (Harvey, *Tanning Materials*, p. 92) found a difference of 1–1·5 per cent. between the lower and upper parts of a plant.

But the above two considerations are rarely taken into account by the contractors who collect the bark and hence the supply of poor grade of bark to the tanners.

Extraction.—The tannin present in Avaram belongs to the catechol group and is fairly easily extracted by water. The temperature of water for extraction has been worked out by Mehd and later, by Seshachalam Choudary and Yoganandam (*loc. cit.*), who found that the maximum percentage of tannins was extracted at 95°–100°, and thus concluded this range to be the optimum temperature for extraction of Avaram bark. The preliminary experiments carried out in the present investigation confirmed these results.

About 300 lbs. of bark were extracted with water between 95°–100°C. by the open-vat system. The leaching tanks were made of copper, each measuring about 22″ in diameter and 23″ in height, capable of holding about 50 lbs. of crushed bark together with about 20 gallons of water. They were also fitted with outlet taps very near the bottom on the side, and in order to prevent the taps being choked up by the crushed bark, a perforated false bottom was placed inside the vessel about 2″ from the bottom. Heating was done by steam, and as copper tubes are expensive, lead tubes (5/8″ diameter, 34′ in each tank) were used instead and were quite satisfactory. It was found in practice that the liquor could be heated up to 95°C. in about 15 minutes. A battery of four such vats was arranged and each charge of water worked through the whole series in such a way that stronger liquors passed through fresher bark, yielding in the end a fairly concentrated liquor. Six leachings, each extending to about 20 minutes, were found necessary to exhaust each charge of bark. The warm liquors were drawn out through the outlets and were fairly clear having been filtered through the column of the bark. But while attempting further clarification by sedimentation, it was observed that a good quantity of solid deposited at the bottom of the vessel and was found to contain some tannin. This must have been the difficultly soluble tannin which separated out on cooling the liquor.

But it was observed that the liquor thus obtained was particularly dark in colour. This was surprising in view of the experiments of Seshachalam Choudary and Yoganandam (*loc. cit.*). Their figures indicate that the colour is maximum when extraction is carried out at lower temperatures and is much lighter at higher temperatures.

Further preliminary experiments carried out, in order to find the best conditions for getting light-coloured liquor, suggested the employment of lower temperatures for the extraction of the major portion of the tannin, heating the fresh water to about 95°C. being resorted to only to extract the last portions of tannin. These results are in entire agreement with the statements made by Wilson (*Chemistry of Leather Manufacture*, Vol. 1, pp. 409–415): "The rate at which tannin can be extracted from the raw material increases with the temperature of the water used, but so also does the rate at which the dissolved matter decomposes. It is customary to extract the fresh material at a low temperature and to increase the temperature of extraction until the material is practically exhausted. In using the open-vat system for ordinary barks, it is a good plan to have the fresh water at the boiling point and to allow its temperature to fall slowly to about 60°C. as it passes over the fresher bark." This prevents to a certain extent the decomposition of tannin and darkening of colour of the liquor.

The method of extraction was, therefore, modified. The successive extractions were carried out with water at temperatures of 50°, 60°, 70°, 80°, 90° C. and finally with boiling water. The time of leaching also ranged from one hour for the first leaching to about quarter of an hour with boiling water. By this modification, the amount of extracted matter (as determined by the total soluble solids in the liquor) amounted to roughly 95 per cent. of extractable matter in the bark as against only 80 per cent. extraction by the previous method. There was decided improvement in the colour of the liquor.

Even this liquor when concentrated as described later and used for tanning did not give satisfactory results. Besides the control of the temperatures in the different stages of extraction, the one other factor in extraction, which affects the colour of the liquor, is the pH value of the water. The work of Wilson and Kern (*Chemistry of Leather Manufacture*, Vol. 1, pp. 409–415) has shown that acidified water with a pH value of 5 is better than ordinary water inasmuch as it prevents the oxidation of the tannin effectively; and moreover, tannins are not precipitated by lime when water with a pH value below 7 is used. Water acidified with acetic acid, was, therefore, used for extraction, with some beneficial result.

Decolourisation.—The necessity of improving the colour further was evident. A number of materials like Fuller's earth, kaolin, alum, aluminium sulphate (alone and in conjunction with oxalic acid), soluble albumin, borax, etc., were tried without any appreciable effect. A saturated solution of sulphur dioxide gave better results. To the warm, turbid tan liquor from the leaching tanks, sulphurous acid was added in small quantities at a time with constant stirring, till there was a faint smell of sulphur dioxide. The liquor was stirred for another quarter of an hour and allowed to settle. The quantity of sulphurous acid required varies with concentration, temparature, etc., of the liquor, but usually 200-350 c.c. of a saturated solution for every 50 gallons of tan liquor were found sufficient. It is well known that sulphur dioxide not only lightens the colour of the liquor, but also helps the dissolution of the difficultly soluble tannins which otherwise would be lost by precipitation. In illustration, an extract liquor in which the ratio, tans/non-tans was 6·8/8·9, *i.e.*, < 1, after being treated with sulphur dioxide, analysed to 9·7/5·2, *i.e.*, > 1. In the untreated extract liquors, a considerable quantity of tannin is lost by precipitation during clarification, and this loss is prevented by sulphur dioxide.

The growth of molds in tan liquors is very common when kept even for two or three days. It is, therefore, usual to employ inhibitors like thymol, phenol, formic acid, etc. In the present investigation, it was noticed that sulphur dioxide itself prevented the growth of molds effectively and no other inhibitor was found necessary.

It may be mentioned that a solution of sulphur dioxide was used in preference to sodium bisulphite as the effect of the latter was found to be more of solubilising than of decolourising.

Concentration.—From the laboratory experiments carried out in the present work, it was found that a solid extract analysing to: tannins 45 per cent., non-tannins 23 per cent., insolubles 13 per cent. and water 19 per cent., was not quite satisfactory, the percentage of insolubles being too high. Besides, it was not readily soluble in cold water; hard lumps or cakes were formed when the extract was mixed with water and dissolution was slow even with agitation. It was, therefore, decided to concentrate the liquor to a soft extract.

The apparatus employed was the Laboratory Vacuum Film Evaporator described by Watson (*J. Indian Inst. Sci.*, 1919, **2**, pp. 209-212). The effective length of the tube was 12 ft. and the separator measured 6″ x 8″; the helical beffle was found unnecessary. The evaporative capacity of the tube was 10-15 litres of water per hour under a pressure of 100-200 mm. of mercury, using steam at 25-30 lbs. pressure.

From the preliminary experiments with this evaporator, it was found convenient to concentrate the liquor to a soft extract in two stages instead of one. The first stage consisted tan liquor roughly from 5 to 1 by volume. This gave a fairly thick liquid which analysed to : tannins 19·0 per cent., non-tannins 14·5 per cent., insolubles 2·5 per cent. and water 64·0 per cent. This was again fed into the evaporator and further concentrated to an extract, which, while warm, was sufficiently mobile to flow from the separator into the receiver. The ratio of extract to water distilling off in this second stage was approximately 1 : 3 by volume. The average sample of the soft extract obtained was analysed and found to contain tannins 35 per cent., non-tannins 28 per cent., insolubles 3 per cent. and water 34 per cent. In later experiments, it was found possible by further concentration to obtain extracts having a tannin-content of 38 per cent.

Tanning.—The tanning was carried out in the local tannery by the tanners and the process of tanning was similar to the one in use in bark-tanning.

It is customary to carry out tanning with Avaram bark in three stages, each for a period of 7-8 days; a final finish with myrobalams is then given. The same method was adopted with the extract also. The quantity of extract employed in each stage was corresponding to the amount of tannins made use of, from each charge of bark. From the following figures,

	Tannins	Non-tannins
Fresh Avaram bark ..	11·8	13·1
Spent Avaram bark ..	5·6	9·7

it will be seen that only about half the quantity of tannins contained in the bark is made use of, the rest being wasted in the "spent" bark. This available percentage of tannins is higher the better the quality of bark employed. By knowing the quantity of bark employed in each stage, the amount of tannins actually used up was calculated and the quantity of extract to be used was determined from these data.

The extract prepared from liquors when leaching was carried out at 95°–100°C., produced very dark-coloured leather. There was no doubt that the extract was quite unsuitable if colour, a very important factor indeed, is taken into account. An extract by the modified method was found to yield leather of a decidedly lighter shade. But even this was not quite satisfactory; the leather was still red which would certainly darken on exposure. It is expected, however, that the extract prepared from liquors treated with sulphur dioxide would produce leather of a suitable quality.

It was found that, while a period of 22 days is usually required for Avaram bark tanning, the whole process was complete in 13–14 days when extract was used.

Discussion.—There are a number of factors which cause this darkening of the colour of leather. Firstly, the work of Wilson and Kern ("The Colour Value of a tan liquor as a function of pH," *Ind. Eng. Chem.*, 1921, **13**, p. 1025) has proved beyond doubt that the colour of tan liquor, and consequently of leather, depends largely on the pH value of the liquor. It should be maintained as low as possible, usually in the neighbourhood of 4. Increase in the pH value of the liquor while tanning is going on must be checked either by added acids or substances which form acids. In this respect the raw materials have a decided advantage over the extracts. They contain more or less quantities of fermentable sugars—the quantity varying with different materials—which produce acidic substances while the tanning proceeds. This automatically maintains the acidity of the liquors in the vats fairly steady. In the case of extracts, on the other hand, these sugars are destroyed during concentration of the liquors and the pH value of the liquor increases very rapidly thereby affecting the colour of the leather seriously. It is hoped to prevent this destruction of acid-producing materials in future experiments.

TABLE II.

Avaram Extract.

		pH value
Fresh liquor	..	4.4
After 1 day	..	4·6
,, 2 days	..	4·8
,, 3 ,,	..	5·6

Before tanning experiments were done, day-to-day analyses of the vat liquors of Avaram bark, and incidentally of Wattle bark also were carried out in order to be able to carry out extract-tanning under similar conditions.

TABLE III.

Avaram Bark Liquors.

Time	pH	Percentages		
		Sol. Solids	Non-tans	Tannins
Fresh liquor ready for use ..	4·4	1·9	0·9	1·0
With leather for 1 day ..	4·5	1·5	1·0	0·5
,, ,, 2 days ..	4·6	1·4	1·2	0·2
,, ,, 3 ,, ..	4·6	1·3	1·2	0·1
,, ,, 4 ,, ..	4·6	1·4	1·2	0·2
,, ,, 5 ,, ..	4·6	1·3	1·3	0·0
,, ,, 6 ,, ..	4·7	1·2	0·9	0·2
,, ,, 7 ,, ..	4·7	1·1	0·7	0·4
,, ,, 8 ,, ..	4·6	1·1	0·5	0·7
Spent liquor	4·6	1·0	0·8	0·2
2nd stage tan liquor ..	4·4	1·4	0·8	0·5
,, ,, for 10 days ..	4·4	1·3	1·0	0·3
,, ,, ,, 11 ,, ..	4·6	1·3	1·0	0·2

TABLE IV.

Wattle Bark Liquors.

Time	pH	Percentages		
		Sol. Solids	Non-tans	Tannins
Tan liquor for fresh leather: fresh water *plus* spent liquor with bark for 24 hours ..	4·4	1·7	0·8	0.9
After 1 day with skin ..	4·5	1·6	0·9	0·7
„ 2 days ..	4·7	1·7	1·1	0·6
„ 3 „ ..	4·7	1·5	1·2	0·3
„ 4 „ ..	4·7	1·4	1·0	0·4
„ 5 „ ..	4·9	1·3	1·1	0·2
„ 6 „ ..	5·2	1·7	1·2	0·5
„ 7 „ ..	5·0	1·3	1·1	0·2
„ 8 „ ..	5·4	1·2	1·2	0·0
Spent liquor ..	5·2	1·3	1·1	0·2
Fresh bark after 1 day ..	4·4	0·9	0·4	0·5
After 10 days ..	4·7	1·5	0·8	0·6
„ 11 „ ..	4·4	1·4	0·7	0·7
„ 12 „ ..	4·4	1·1	0·8	0·5
„ 13 „ ..	4·4	1·1	0·8	0·3

From the above two tables, it is clear that the pH value increases slowly from 4·4 to 4·7 (in the case of Avaram) and from 4·4 to 5·4 (in the case of Wattle) during the period of a week. This is certainly slow compared with the rate of increase in extract liquors (Table II).

The addition of suitable acids or acid-forming substances to the extract or to the extract liquors is, therefore, a matter of necessity. The first alternative which suggests itself is the preparation of mixed extracts from Avaram and other suitable tanning agents.

Secondly, the method and rate at which the tanning proceeds seems to be another factor affecting the colour and softness of the leather. From Tables III and IV, it is clear that the concentration of tannin in the vat liquor is rarely more than 1 per cent. Since cold water can extract the tannins from the raw material only very slowly, small quantities of tannins are available, at any given time, for the hides to absorb. In the case of extracts, all the tannin is in a readily soluble form. The rate at which tannins penetrate into the pores of the hides is, therefore, very much greater than the rate at which they form insoluble hide-tan substances. This results in some tannin being merely mechanically held in the pores of hide and therefore easily oxidised, changing thereby the colour of the leather to a darker shade.

The leather, produced by rapid tanning, was also much harder than ordinary bark-tanned leather.

CONCLUSION.

In view of these considerations and experimental results, it looks improbable that Avaram extract alone is suitable for tanning, particularly by the old-fashioned methods prevalent in our tanneries. Mixed extracts will be prepared and tried. There are a number of tanning agents like Myrobalams, Divi-divi, *Cassia fistula*, and *Anogeissus latifolia*, fairly rich in sugars and which, besides, are known to produce light coloured leathers (due to the nature of tannins present). It is proposed to use these materials in conjunction with Avaram extract or even extracts of these materials with Avaram extract. Also, it is absolutely necessary to work out the method of using these extracts, since any slight variation in the process of tanning with them is likely to yield bad results. It is proposed to continue the work in the direction mentioned above.

SUMMARY.

Extract of Avaram has been prepared on a semi-commercial scale and used in local tanneries. It has been found fairly satisfactory, except for one or two defects, which it is hoped to overcome.

Useful data on the changes occurring in the vat-liquor during tanning have been collected and recorded.

This work was done for the Government of Mysore, whom we wish to thank for granting scholarships to both of us. In conclusion, we have great pleasure in thanking Dr. H. E. Watson for his kind interest in this investigation and Mr. B. V. Ramiengar, Chief Conservator of Forests, for placing at our disposal the resources of his Department and for advice.

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ESTIMATION OF POTASSIUM BY THE COBALTINITRITE METHOD.

By S. D. Sunawala and K. R. Krishnaswami.

The cobaltinitrite method for the estimation of potassium has been investigated by several workers of whom the following might be mentioned. Addie and Wood (*J.C.S.*, 1900, **77,** 1076) studied the method in detail and found that the precipitate of potassium-sodium cobaltinitrite obtained had the formula $K_2NaCo(NO_2)_6.H_2O$, and that potassium could be estimated gravimetrically or volumetrically either by weighing the precipitate as such or by determining the NO_2 in it by titration with standard permanganate. They also found that the results obtained by the cobaltinitrite method were just as accurate as those obtained by the perchlorate method for the estimation of potassium. Cunningham and Perkin (*J.C.S.*, 1909, **95,** 1568) observed in the course of their work on organic cobaltinitrites that the estimation of potassium as potassium-sodium cobaltinitrite was unsatisfactory as the precipitate could not be washed and filtered properly owing to its tendency to become colloidal on washing. Vürtheim (*Rec. trav. chim.*, 1921, **40,** 593) found that the formula of precipitated potassium-sodium cobaltinitrite was $K_{1.5}Na_{1.5}Co(NO_2)_6.nH_2O$, as had been previously suggested by Gilbert (*Z. anal. Chem.*, 1891, **38,** 184). This, however, was disproved by Bonneau (*Bull. Soc. Chim.*, 1929, **46,** 798) who at the same time confirmed the results obtained by Addie and Wood (*loc. cit.*) and showed that the number of water molecules attached to $K_2NaCo(NO_2)_6$ is usually one. According to him the composition of the precipitate depends on the ratio of the concentrations of sodium and potassium in the reaction mixture. Druschel (*Z. anorg. Chem.*, 1908, **56,** 223) effected some modifications in the procedure suggested by Addie and Wood (*loc. cit.*) and obtained satisfactory results by the volumetric method. On the other hand, Strecker and Junck (*Z. anal. Chem.*, 1923, **63,** 161) who carried out a comparative study of a number of methods of estimating potassium found that the precipitation of potassium as cobaltinitrite did not lead to concordant results, because, although the precipitation was complete, the composition of the precipitate varied considerably in different experiments. They therefore recommended the precipitation of potassium by addition of sodium cobaltinitrite and the subsequent determination of the potassium in the precipitate by the perchlorate method. Hamid (*Analyst*, 1926, **51,** 450) made some determinations of potassium by the cobaltinitrite as well as by the perchlorate method and found that the results obtained by the two methods were in satisfactory agreement.

Wasselieef and Matwejeb (*Z. anal. Chem.*, 1930, **81,** 106) carried out a detailed study of the method on the basis of which they suggest a procedure for obtaining satisfactory results. In order to reduce the time necessary for the coagulation of the precipitate and thereby hasten the estimation of potassium, Grigoriev and Karol (*J. Chem. Ind.*, Moscow, 1931, **8,** 68: *cf. Chem. Abstr.*, 1931, 700) recommend the evaporation of the reaction mixture almost to dryness, diluting with water and filtering immediately.

This work was undertaken with a view to exploring the various sources of error and to determine the conditions necessary for getting accurate results. Trials were made of the various methods outlined above and it was found that the procedure recommended by Wasselieef and Matwejeb (*loc. cit.*) was the most reliable. This was the case, however, only when definite quantities of the reagents were employed, excess or deficit in the quantity of sodium nitrite added yielding results which were too high and too low respectively, if calculations were always based on the formula $K_2NaCo(NO_2)_6,H_2O$. We found that this was due to the fact that the number of water molecules in the precipitate was either ½, 1, or 2 depending on the conditions of precipitation, all these three hydrates being quite stable at the temperature employed for drying, *viz.*, 100–110°. In order to overcome this complication we devised the method described in a later part of this paper and found it satisfactory.

EXPERIMENTAL.

The potassium salts employed in the investigation were either purified for the purpose or were pure analytical preparations of Kahlbaum. The procedure required to be followed in order to get accurate results was experimentally worked out and found to be as follows. Known quantities of the potassium salt were dissolved in 5 c.c. of water, acidified with 1–2 c.c. of acetic acid and the required quantities of sodium nitrite (50 per cent. solution) and cobalt sulphate (25 per cent. solution) were added. The mixture was then heated on a water-bath for about 5′, and then kept aside to settle for about 16 hours. It was then filtered through a weighed gooch crucible, the precipitate being washed with 50–75 c.c. of cold water, first by decantation and then on the filter. The precipitate was dried at 110° to constant weight. From the weight of the precipitate obtained, the quantity of potassium was calculated assuming that the precipitate had the formula $K_2NaCo(NO_2)_6,H_2O$. The results obtained by employing this procedure are given in Table I.

Equal quantities of the solutions of sodium nitrite (50 per cent.) and cobalt sulphate (25 per cent.) were always added, the quantities employed in the analysis of 0·05, 0·1, 0·2, 0·3, 0·5 and 1·0 g. of potassium nitrate being 1, 2-3, 6-7, 10-11, 15-17 and 25-27 c.c. respectively of each solution.

TABLE I.

KNO_3		Error per cent.	KNO_3		Error per cent.	KNO_3		Error per cent.
taken g.	found g.		taken g.	found g.		taken g.	found g.	
0·0500	0·0497	−0·6	0·2000	0·2006	+0·3	0·5000	0·4980	−0·4
,,	0·0499	−0·2	,,	0·2002	+0·1	,,	0·4970	−0·6
,,	0·0498	−0·4	,,	0·1992	−0·4	,,	0·5015	+0·3
,,	0·0502	+0·4	,,	0·1994	−0·3	,,	0·5020	+0·4
0·1000	0·1005	+0·5	,,	0·2010	+0·5	,,	0·4995	−0·1
,,	0·0993	−0·7	,,	0·1996	−0·2	1·0000	1·0030	+0·3
,,	0·1003	+0·3	0·3000	0·2997	−0·1	,,	0·9962	−0·4
,,	0·1007	+0·7	,,	0·3009	+0·3	,,	0·9952	−0·5
,,	0·0999	−0·1	,,	0·2994	−0·2	,,	1·0030	+0·3
,,	0·0999	−0·1	,,	0·2994	−0·2	,,	0·9922	−0·8
			,,	0·3010	+0·3	,,	0·9992	−0·1

It is seen from Table I that all the results given are accurate to within 1 per cent. This, however, was found to be the case only when the specified quantities of the reagents were added. Addition of the proper quantity of cobalt sulphate but different quantities of the sodium nitrite reagent led to inaccurate results as is shown in Table II.

The results given in Table II indicate that addition of a smaller quantity of reagent than that required (3 c.c. for 0·1 g. and 7 c.c. for 0·2 g. KNO_3) yields results which are low whereas addition of excess leads to results which are high. Similar variations in the quantity of cobalt sulphate employed were found to have no effect on the accuracy of the determinations. Since it was found that the low results shown in Table II were *not due to incomplete precipitation*, it was thought that they were due to formation of precipitates other than $K_2NaCo(NO_2)_6$, H_2O. Hence a close study of these precipitates was undertaken by collecting them in sufficient quantities and analysing them. Of the various precipitates collected and analysed, only three will be mentioned here as the others were probably only mixtures of these in various proportions. The three types were those which yielded values for potassium which were (*a*) accurate, (*b*) 2 per cent. too low, and (*c*) 4 per cent. too high respectively when calculated on the basis of the formula

TABLE II.

KNO_3 taken g.	$NaNO_2$ added c.c.	KNO_3 found g.	Error per cent.	KNO_3 taken g.	$NaNO_2$ added c.c.	KNO_3 found g.	Error per cent.
0·1000	2	0·0992	−0·8	0·2000	4	0·1928	−3·6
,,	3	0·0998	−0·2	,,	4·5	0·1940	−3·0
,,	4	0·1017	+1·7	,,	5	0·1958	−2·1
,,	5	0·1020	+2·0	,,	5·5	0·1970	−1·5
,,	6	0·1023	+2·3	,,	6	0·1982	−0·9
				,,	6·5	0·1984	−0·8
					7	0·1990	−0·5
					7·5	0·2016	+0·8
					8	0·2036	+1·8
					9	0·2058	+2·9

$K_2NaCo(NO_2)_6,H_2O$. The analysis of the precipitates consisted in the estimation of potassium, sodium, cobalt, "NO_2", and water by the methods given below.

Estimation of sodium and potassium.—A known quantity of the precipitate was ignited in a porcelain crucible and the mass digested with water when black oxide of cobalt separated and the alkali salts went into solution. It was then filtered and the residue thoroughly washed with hot water. The filtrate was then evaporated in a silica dish and the sodium and potassium weighed together as chlorides. Potassium was then estimated by the perchlorate method and the sodium obtained by difference.

Cobalt.—About 1·5 g. of the substance was dissolved in sulphuric acid (1 : 4) and the oxides of nitrogen driven off by boiling. The solution was first neutralised with dilute ammonia after which 5 g. of ammonium sulphate and 50–60 c.c. of conc. ammonia were added. This solution was electrolysed employing a current-density of 0·5–0·7 Amp./sq.dm., and an E.M.F. of 2·8–3 volts. The cylindrical platinum gauze cathode was rotated by an electrically driven motor, the speed of which could be varied from 100–2000 revolutions per minute. It was found that the period necessary for the complete deposition of cobalt was considerably shortened by the addition of some sodium bisulphite (0·2–0·4 g.) as suggested by Brophy (*Ind. Eng. Chem. Anal.*, 1931, **3**, 363).

NO_2.—This estimation was always done by the permanganate oxidation method, and in some cases also by the nitrometer method due to Dumas. In the former method the substance (0·2 g.) was boiled with sodium hydroxide (30 c.c. 10 per cent. sol.), and the cobalt hydroxide which separated was filtered off. The filtrate and washings were diluted with water to about 400 c.c., acidified with sulphuric acid and titrated with N/10 $KMnO_4$. As this procedure leads to low results owing to loss of oxides of nitrogen during the process of neutralization with sulphuric acid, it was modified as follows. To the filtrate and washings containing the nitrite, N/10 $KMnO_4$ was added in such a quantity as was insufficient by about 1 c.c. to effect complete oxidation. It was then acidified with sulphuric acid and the titration completed with N/10 $KMnO_4$. The results obtained by this method were in good agreement with those obtained by the method of Dumas.

Water.—Owing to the low water content of the precipitates analysed, fairly large samples (1·5 g.) had to be employed. The weighed sample was kept in a porcelain boat in a combustion tube connected at one end with a carbon dioxide Kipp's apparatus through drying vessels containing sulphuric acid and phosphorus pentoxide. Freshly reduced copper gauze was kept heated at the other end of the combustion tube in order to reduce the oxides of nitrogen given off by the substance on heating. The water vapour evolved was collected and weighed in a calcium chloride U tube which was protected from atmospheric moisture by suitable guard tubes. The substance was introduced into the combustion tube after the apparatus had been thoroughly dried in a stream of dry carbon dioxide. All the precautions usual in such determinations were duly observed.

The results of analyses of the various precipitates are assembled together in Table III, each result being the mean of three or four concordant determinations.

TABLE III.

	K	Na	Co	NO_2	H_2O
Ppt. which yielded low results ..	17·7	5·5	13·1	61·9	1·8
$K_2NaCo(NO_2)_6$, $\frac{1}{2}$ H_2O requires ..	17·6	5·2	13·2	62·0	2·0
Ppt. which yielded accurate results ..	16·9	5·3	13·1	60·8	3·8
$K_2NaCo(NO_2)_6$,H_2O requires ..	17·2	5·1	13·0	60·8	3·9
Ppt. which yielded high results ..	16·6	4·9	12·8	58·8	6·9
$K_2NaCo(NO_2)_6$, $2H_2O$ requires ..	16·6	4·9	12·8	58·6	7·2

The results given in Table III indicate that whereas the precipitate which yields accurate results corresponds to the formula $K_2NaCo(NO_2)_6,H_2O$, those which gave low and high results correspond to $K_2NaCo(NO_2)_6, \frac{1}{2} H_2O$ and $K_2NaCO(NO_2)_6, 2H_2O$ respectively. It is evident therefore that incorrect results would be obtained if the precipitate is always assumed to have the formula $K_2NaCo(NO_2)_6, H_2O$. It has been shown already (Table II) that correct results can be obtained, *i.e.*, potassium precipitated as $K_2NaCo(NO_2)_6,H_2O$ only when the quantities of reagents added, strictly correspond to the quantity of potassium present in the solution. It therefore appeared to us that the accurate estimation of the potassium content of a mixture could be carried out as follows. The sample is brought into solution and assuming that it consists almost entirely of a salt of potassium the corresponding quantities of reagents are added, the details of the procedure being as outlined on p. 3. From the weight of the precipitate obtained, the potassium content of the mixture is calculated, and as this value is about 5 per cent. too high, the actual potassium content of the mixture is arrived at approximately. So, another lot of the mixture is weighed out, brought into solution and such quantities of the reagents are added as correspond to the potassium content deduced as mentioned above and the determination carried out as described already. In case, however, the stock of mixture is insufficient for several analyses, the precipitate obtained in the preliminary estimation in which excess of the reagents were added can be utilised in place of a fresh lot of mixture as follows. The precipitate is dissolved in hydrochloric acid (5 p.c.), the excess of acid expelled by evaporating the solution to dryness, and the residue taken up with water and filtered. Since the potassium content of the filtrate is known approximately, it is relatively simple to carry out the determination by the procedure described earlier. The results of some determinations carried out by this modified procedure are given in Table IV.

All the results shown in Table IV are accurate to within 1 per cent. thus indicating that the procedure outlined above is reliable. Parallel estimation of potassium in some mixtures was then conducted by this method as well as by the perchlorate method as recommended by Treadwell (*Analytical Chemistry*, **II**, 1930, 64). The results obtained are given in Table V, and it can be seen that they are in fair agreement.

The next point studied was the solubility of potassium-sodium cobaltinitrite in water at different temperatures. A weighed quantity (2 g.) of the substance was added to 100 c.c. of water contained in a round bottomed flask which was kept in a water bath maintained at the desired temperature ±1°. The contents of the flask were stirred vigorously for about two hours, after which it was filtered through a weighed gooch crucible and the solid collected was weighed. This

TABLE IV.

Mixture	KNO_3 per cent.	Actual per cent.	Error per cent.
$KNO_3 + MgO$	66·8	66·7	−0·2
,,	66·9	66·7	−0·3
,,	50·3	50·0	+0·6
$KNO_3 + NaCl$	66·8	66·7	+0·3
,,	49·9	50·0	−0·2
$KNO_3 + Na_2HPO_4$	49·8	50·0	−0·4
,,	49·7	50·0	−0·6
$KNO_3 + NaCl + Fe_2O_3 + Al_2O_3 + SiO_2 + CaO + MgO$	33·2	33·3	−0·3
,,	33·3	33·3	0·0
,,	33·5	33·3	+0·6
,,	22·4	22·3	+0·5
,,	22·4	22·3	+0·5
,,	10·25	10·16	+0·9
,,	10·15	10·16	−0·1

TABLE V.

KNO_3 actually present ..	22·30	22·30	10·76	10·76	per cent.
KNO_3 found by cobaltinitrite method	22·44	22·47	10·82	10·83	,,
KNO_3 found by perchlorate method	22·49	22·40	10·85	10·86	,,

weight when deducted from the weight of the solid originally taken gave the quantity of the solid which went into solution. In some cases a control determination of this quantity was made by evaporating the filtrate to dryness in a small silica dish and weighing the solid recovered. Measurements of solubility could not be made at temperatures exceeding 60° as the precipitate decomposed during the experiments at those temperatures. Attempts were not made to obtain very accurate figures as the solubility was found to be small. The results obtained are given in the table below.

TABLE VI.

Temperature ..	20	25	30	40	50
Solubility in mg. per 100 c.c. of water ..	1	3	9	21	60

It should be noted that the data shown above were obtained by stirring the substance vigorously for two hours in water at the required temperature. In actual estimations of potassium, however, the precipitate was in contact with water at 25–30° for not more than 20–30 minutes, and it was found that the solubility of the precipitate under such conditions was negligible.

SUMMARY.

Precipitates of potassium-sodium cobaltinitrite obtained under varying conditions were analysed and found to belong to three classes (*a*) $K_2NaCo(NO_2)_6,H_2O$, (*b*) $K_2NaCo(NO_2)_6,\frac{1}{2}H_2O$, and (*c*) $K_2NaCo(NO_2)_6,2H_2O$. Since it is assumed that the precipitate obtained is (*a*) serious errors arise whenever (*b*) or (*c*) is present. A procedure has been suggested by which the precipitation of potassium as (*a*) can be ensured and accurate results obtained.

We wish to express our gratitude to Professor H. E. Watson for his constant interest and helpful criticism during the progress of this investigation.

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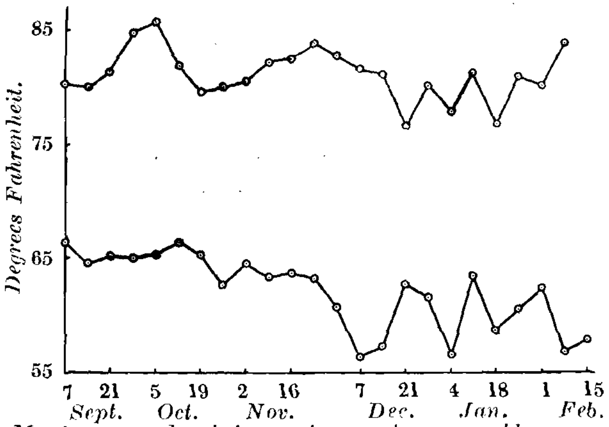
ON THE NATURE AND EXTENT OF PERIODIC FLUCTUATIONS IN CERTAIN SOIL CONSTITUENTS.

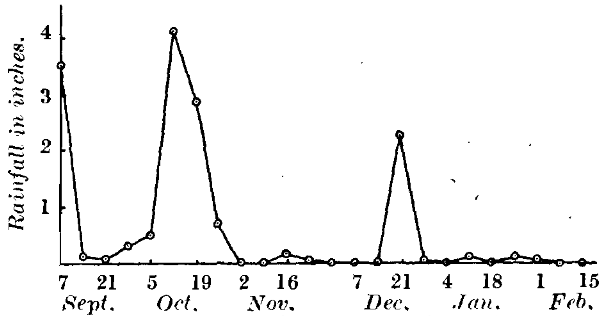
By A. Sreenivasan and V. Subrahmanyan.

During recent years, several investigators have drawn attention to periodic fluctuations in different soil constituents such as organic matter, total nitrogen, nitrates and microbial numbers. Russell (*J. Agric. Sci.*, 1914, **6,** 18) observed that the nitrate content of arable land fluctuates regularly, the changes being more marked in loamy soils than in clays or sands. Prescott and Piper (*J. Agric. Sci.*, 1930, **20,** 517) noted that such variations depend on season, temperature, rainfall, moisture content of soil and other factors. Waksman (*Soil Sci.*, 1916, **1,** 363) found that bacterial numbers varied from time to time, in different seasons and at different depths of soil. Russell and Appleyard (*J. Agric. Sci.*, 1917, **8,** 385) observed similar fluctuations in English soils. Cutler and his associates (*Ann. Appl. Biol.*, 1920, **7,** 11; *Phil. Trans.*, 1922, **B 211,** 317) recorded striking variations in the daily counts of bacteria and certain species of flagellates. Smith and Worden (*J. Agric. Res.*, 1925, **31,** 501) observed similar changes in American soil. Further evidence in support of daily and even hourly changes in bacterial numbers and nitrate contents was adduced by Thornton and his associates (*Soil Sci.*, 1927, **23,** 253; *Proc. Roy. Soc.*, 1930, **B 106,** 399). Annet, Iyer and Kayasth (*Mem. Dept. Agric. India, Chem. Ser.*, 1928, **9,** 155) studied the economy of nitrogen in the black cotton soil during different seasons and observed that although the annual loss in the form of nitrate amounted to about 160 lbs. per acre, the total nitrogen still remained unaffected and continued to be practically the same over a period of 25 years. They concluded, therefore, that there is fixation of nitrogen to compensate for the above loss. The same authors also noted that the total nitrogen contents of dry soils vary from month to month. Sahasrabuddhe and his co-workers (*Mem. Dept. Agric. India, Chem. Ser.*, 1927, **8,** 53; *Ind. J. Agric. Sci.*, 1931, **1,** 631; *ibid.*, 1932, **2,** 455) observed that recuperation of nitrogen in the soils of the Bombay Deccan proceeds continuously and is facilitated by a number of factors, such as wetting followed by dry weather, better cultivation or addition of organic manures. They hold the view that the nitrogen content of soil is not a stable or constant quantity; there is a range for every soil which is determined by various factors such as moisture, temperature and aeration.

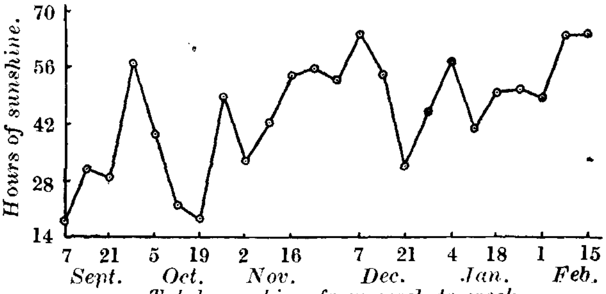
Although the foregoing observations are of considerable practical interest, yet very little is known regarding the chemical and biological



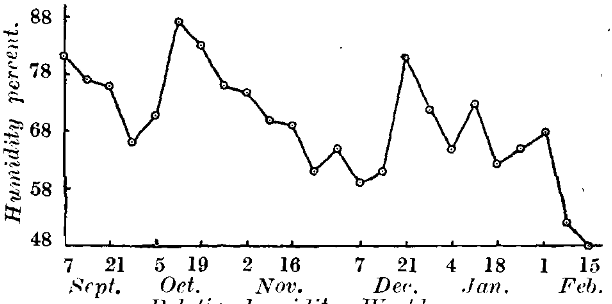
Maximum and minimum temperatures—weekly average.



Total rainfall from week to week.



Total sunshine from week to week.



Relative humidity—Weekly averages.

Fig. 1.

Meteorological Observations.

mechanism of the related processes. Some of the changes, particularly those reported to occur at short intervals, are almost phenomenal, being more rapid than those that could be normally brought about by any combination of chemical and biological agencies known to be associated with the soil. Further knowledge of the nature and extent of the different changes is also needed if they are to be adequately controlled in field practice.

EXPERIMENTAL.

A uniform plot of land measuring 98′ × 49′ was opened up and re-made so as to ensure thorough distribution of soil matter. The weeds were carefully removed and the area divided into 24 plots, each measuring 11′ × 11′ and separated by ridges each 1′ wide and 1′ high. A trench 2′ wide and 2′ deep was dug around the whole area to prevent (*a*) flooding from adjacent areas during rain, and (*b*) encroachment of roots from neighbouring vegetation. The plots were then numbered and given different treatments, the selections being made at random.—(1) Unmanured (control); (2) farmyard manure applied on 9–9–1933 at 3 tons per acre; 5 days later, this was followed by application of superphosphate at 2 cwts. per acre; (3) manured as in (2) and treated with potassium permanganate at 100 lbs. per acre. The last treatment was given as part of a main scheme of investigations on the rôle of oxidising agents as fertilizers. The results of those studies will form the subject of another communication.

Ragi (*Eleucine coracana*) (H_{22} variety) was sown on 18–8–1933. Samples of soil were collected from the various plots at different stages.—(1) Before manuring (8–9–1933); (2) prior to sowing (18–9–1933); (3) seedling stage (3–10–1933); (4) flowering stage (1–11–1933); (5) grain formation (1–12–1933); (6) ripening stage (5–1–1934); and (7) after harvesting (4–2–1934). The samples were collected, with a large cork borer, to a depth of 6″ and the different samples thus collected from each plot, at one time, mixed together and treated as a whole specimen. They were then brought to the laboratory, dried and ground to pass the 30-mesh sieve. Determinations of the different forms of nitrogen were carried out as follows.—Total nitrogen by the Kjeldahl method as modified by Sreenivasan and Subrahmanyan (*Ind. J. Agric. Sci.*, 1933, **3**, 646); ammonia and nitrate according to Olsen (*Compt. rend. Trav. Lab. Carlsberg*, 1929, **17**, No. 15); and organic matter and combined moisture by determining loss on ignition.

*Meteorological Observations.**—Systematic daily records were maintained throughout the period of the investigation. The weekly averages have been presented in Fig. 1.

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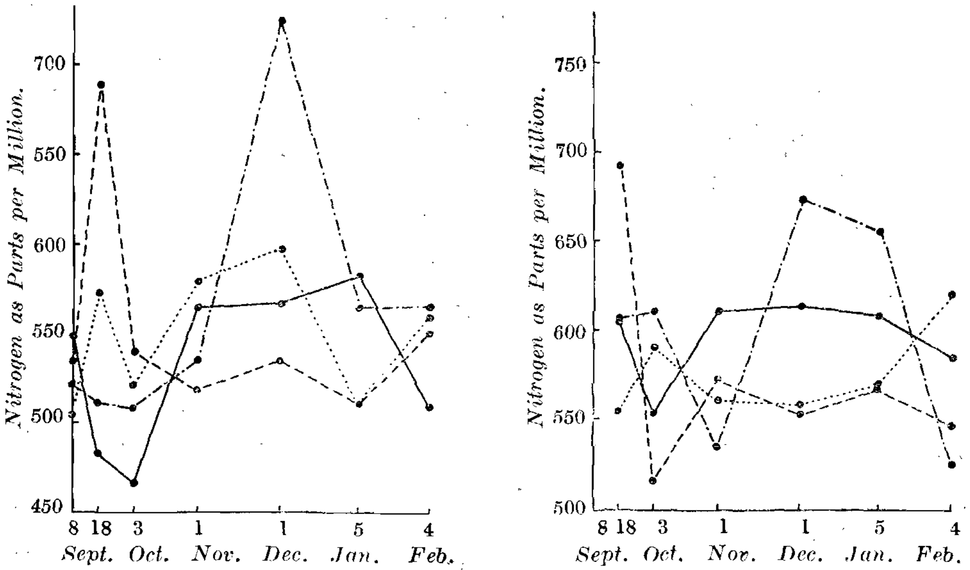
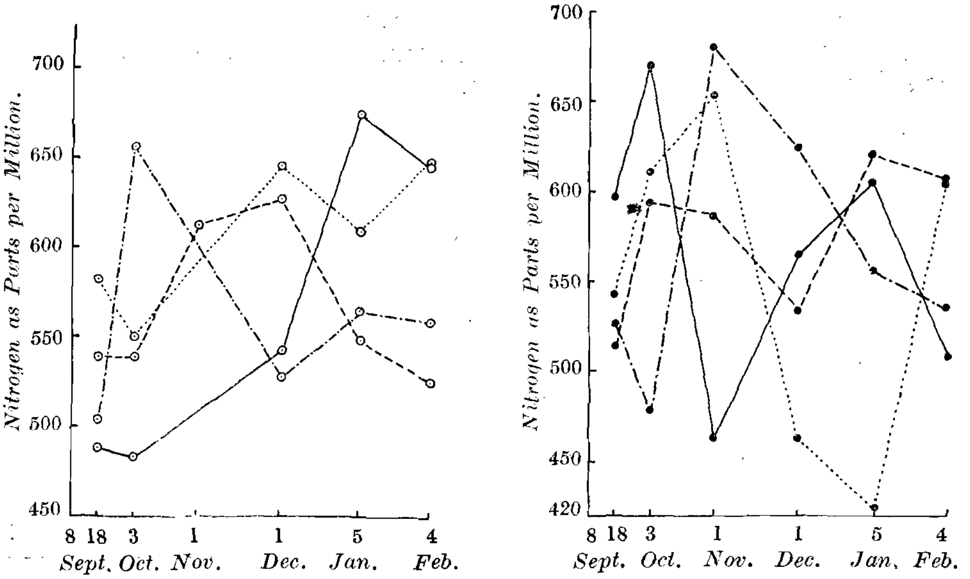
* The data were obtained through the courtesy of the Meteorologist to the Government of Mysore to whom the authors' thanks are due.



Unmanured soil—Plots 1–4.

Manured soil—Plots 1–4.



Manured soil—Plots 5–8.

Manure + Oxidizer—Plots 1–4.

Fig. 2.

Changes in Total Nitrogen.

●——● Plot 1 ○——○ Plot 5
●·····● ,, 2 ○·····○ ,, 6
●– – –● ,, 3 ○– – –○ ,, 7
●—·—● ,, 4 ○—·—○ ,, 8

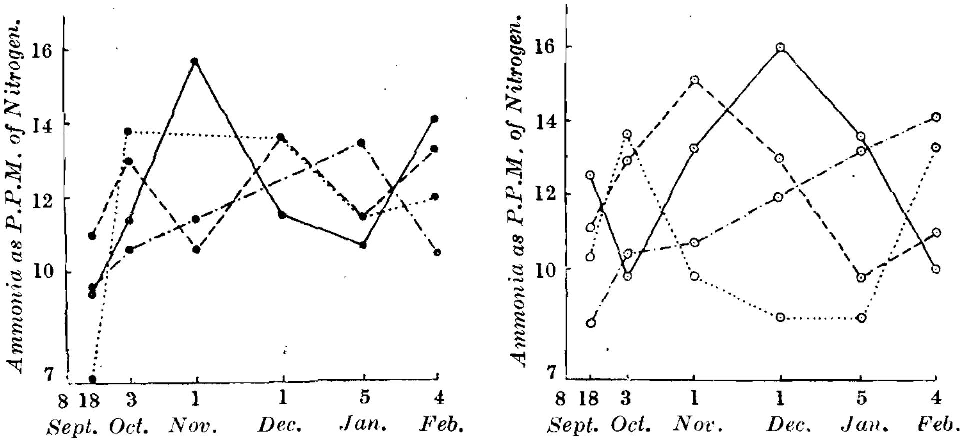
It may be noted that it was fairly warm upto the middle of November after which it turned cool and continued to remain so upto the third week in January when it became warm again. The hours of sunshine bore no relation to changes in temperature. With the exception of the first three weeks in October and a short period during the middle of December, the season was fairly bright and sunny. There were heavy showers early in September just before the commencement of the investigation. There were further periods of heavy rainfall during October and December. The remaining period had either no rains or only occasional, light showers. The relative humidity values followed nearly the same course as the rainfall. Each shower of rain was accompanied by a rise in humidity which was maintained for nearly a week. Succeeding falls caused it to rise again, so that except for a short period between the third week of November and the second week of December, and during early Feburary, the humidity remained consistently above 70 per cent. throughout the period under observation.

Taken as a whole, the observations would suggest that the period of investigation was a moderately wet and humid season with sufficiently long periods of sunshine and fair amount of warmth to favour different types of chemical and biological changes in the soil.

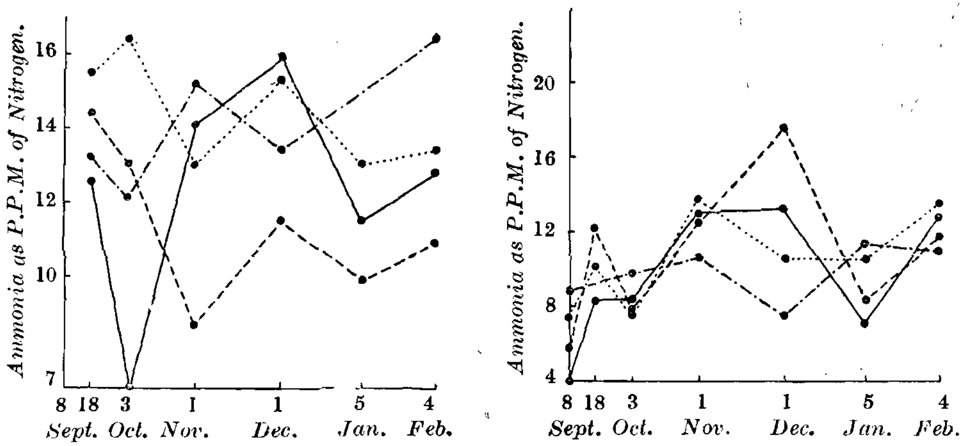
Total Nitrogen.—It may be noted (Fig. 2) that there was considerable fluctuation in nitrogen similar to those recorded by some previous workers. On the other hand, the observations on parallel plots show absolutely no relation to changes in season. Thus, a sudden rise observed in one plot would correspond to no change in a second one, slight depression in a third and marked fall in a fourth. The observations thus show that (*a*) the changes in nitrogen content do not follow any order and (*b*) the results obtained for individual plots at different stages are not significantly different from those in others. It may be further noted that the quantities of nitrogen in the unmanured plots are not appreciably different from those in the manured ones or treated with oxidising agents so that although the added manure enriches the soil with nitrogen, yet the estimates of that constituent have not appreciably improved.

Ammonia.—The changes (Fig. 3) are as varied in character as those observed in the case of total nitrogen. Some of the figures for plots treated with manure and oxidizer are slightly higher than those for others suggesting the production of small quantities of ammonia. No significant difference could be noticed, however, between the other plots or treatments.

Nitrates.—The quantities of nitrates present at any time (Fig. 4) show no relation to either season or treatment. The data for the different plots are of about the same order so that no evidence could be adduced regarding either the production or loss of nitrate under different conditions.



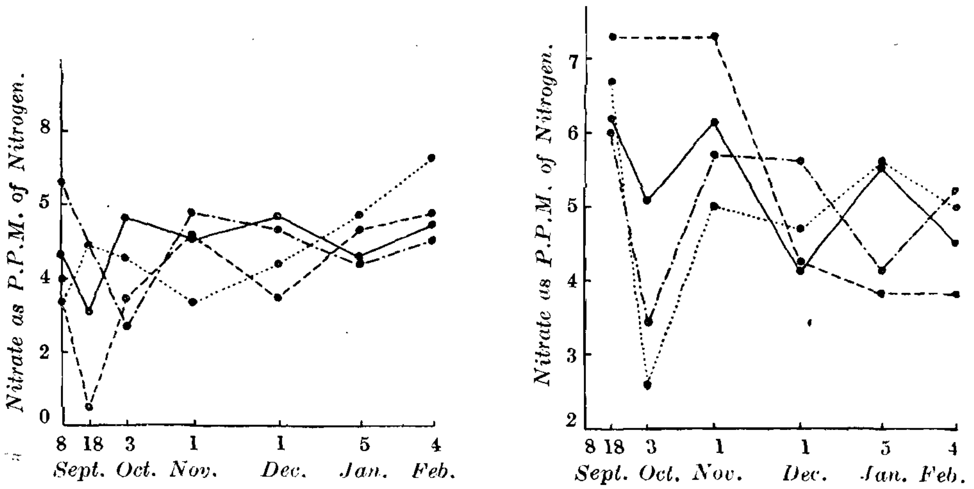
Manured soil—Plots 1-4.   *Manured soil—Plots* 5-8.



Manure + Oxidizer—Plots 1-4.   *Unmanured soil—Plots* 1-4.

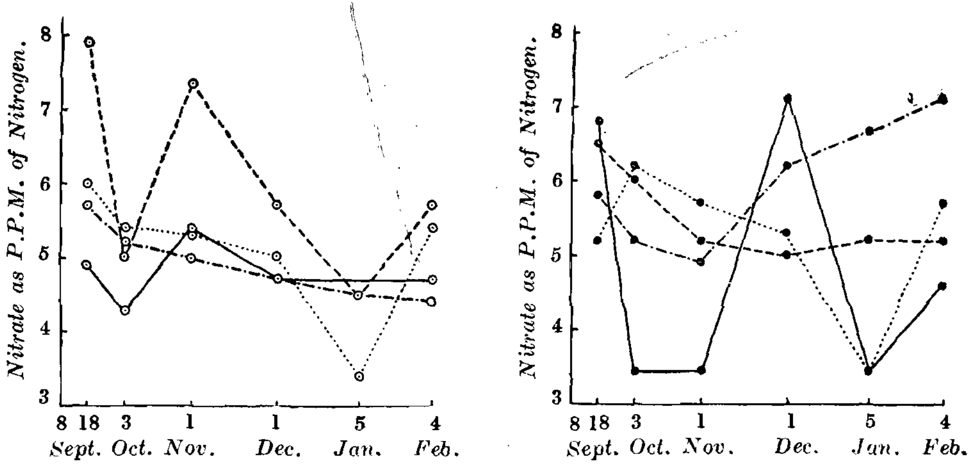
Fig. 3.

Changes in Ammonia Content.



Unmanured soil—Plots 1-4.

Manured soil—Plots 1-4.



Manured soil—Plots 5-8.

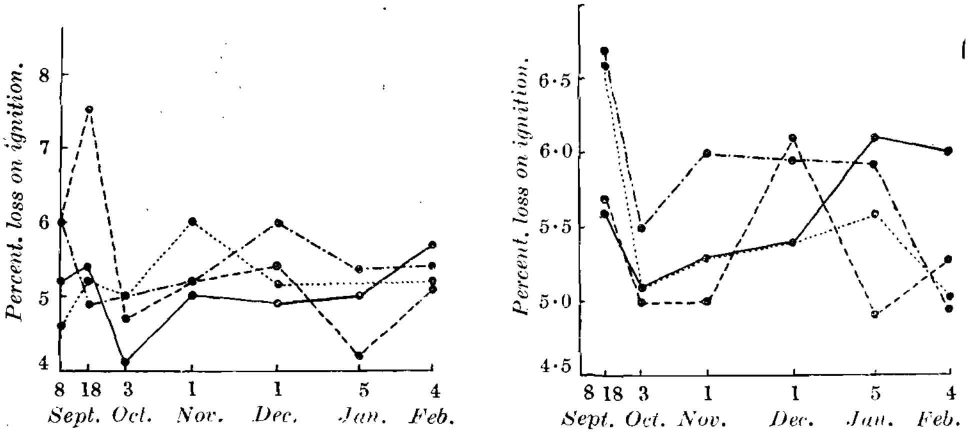
Manure + Oxidizer—Plots 1-4.

Fig. 4.

Changes in Nitrate Content.

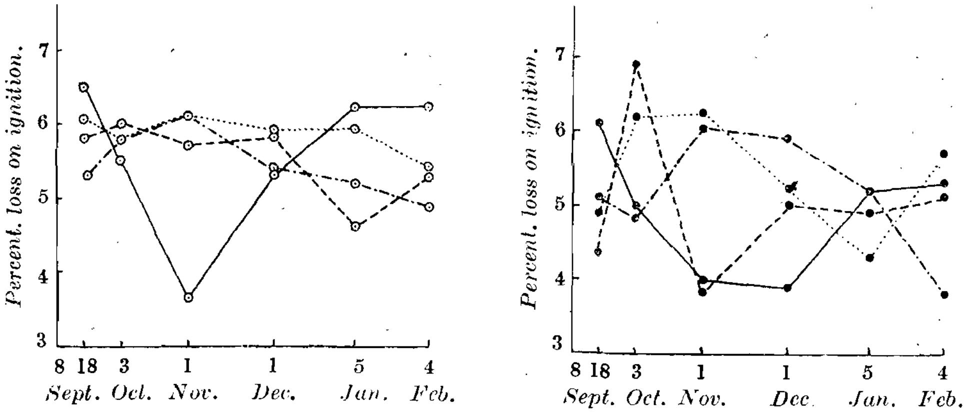
●—● Plot 1
●····● ,, 2
●- - -● ,, 3
●-·-● ,, 4

○—○ Plot 5
○····○ ,, 6
○- - -○ ,, 7
○-·-○ ,, 8



Unmanured soil—Plots 1-4.

Manured soil—Plots 1-4.



Manured soil—Plots 5-8.

Manure + Oxidizer—Plots 1-4.

Fig. 5.

Loss on Ignition.

●—● Plot 1
●····● ,, 2
●- -● ,, 3
●-·-● ,, 4

○—○ Plot 5
○····○ ,, 6
○- -○ ,, 7
○-·-○ ,, 8

Loss on Ignition.—With the exception of a few individual specimens which have yielded abnormally high or low values, all the others come within a narrow range and show no response to either manurial treatment or seasonal changes (Fig. 5).

The average values for the different constituents at various stages as also the corresponding standard deviations were each calculated from 16 sets of determinations in the case of the manured plots and 8 each in those of the others (Table I). The response of the individual plots to different treatments as shown by changes in the chemical constituents was calculated from the results of 14 sets of determinations in each case (Table II). It may be seen that the figures for each constituent are so close and the corresponding standard deviations so large that no significant difference between either different treatments or various plots can be observed.

TABLE I.

Effect of different treatments on certain soil constituents.

Date →	8—9—1933			18—9—1933			3—10—1933		
Treatment→	U	M	M+O	U	M	M+O	U	M	M+O
Total Nitrogen (as p.p.m.) ..	526·8	No treatment	No treatment	563·8	570·8	558·1	508·5	562·1	593·2
Std. deviation ± ..	16·3	..	..	79·2	61·0	44·9	24·3	51·4	69·5
Ammonia nitrogen (as p.p.m.)	7·1	..	..	10·2	9·9	13·9	8·4	11·9	12·1
Std. deviation ± ..	1·7	..	..	1·6	1·6	1·1	0·8	1·5	3·3
Nitrate nitrogen (as p.p m.) ..	5·9	..	..	2·8	6·3	6·1	4·1	5·9	5·2
Std. deviation ± ..	1·8	..	..	1·8	0·9	0·6	1·2	0·8	1·1
Loss on Ignition (as percentage) ..	5·4	..	..	5·8	6·0	5·1	4·7	5·5	5·7
Std. deviation ± ..	0·6	..	..	1·3	0·5	0·6	0·4	0·3	0·9

U = Unmanured. M = Manured. M + O = Manure + Oxidizer.

TABLE I.—(*Contd.*)

Date →	1—11—1933			1—12—1933			5—1—1934			4—2—1934		
Treatment→	U	M	M+O	U	M	M+O	U	M	M+O	U	M	M+O
Total Nitrogen (as p.p.m.) ..	549·5	556·6	600·5	605·4	591·1	551·0	541·8	599·3	557·7	542·7	581·4	569·2
Std. deviation ± ..	24·2	92·3	84·4	72·0	49·6	58·4	31·9	42·9	78·7	25·8	47·3	43·5
Ammonia nitrogen (as p.p.m.)	12·5	12·3	12·8	12·2	12·7	14·0	9·4	11·5	11·5	12·0	12·2	13·4
Std. deviation ± ..	1·2	2·2	2·5	3·7	2·3	1·7	1·7	1·1	1·2	1·5	1·5	2·0
Nitrate nitrogen (as p.p.m.) ..	4·8	4·9	4·8	4·6	4·9	5·9	4·9	4·4	3·9	5·7	4·8	5·7
Std. deviation ± ..	0·9	0·6	0·9	0·9	0·2	0·8	0·2	1·0	0·8	0·8	0·6	0·9
Loss on Ignition (as percentage) ..	5·3	5·4	5·0	5·4	5·7	5·0	4·9	5·6	4·9	5·4	5·0	5·0
Std. deviation ± ..	0·4	0·8	1·1	0·4	0·1	0·7	0·4	0·6	0·4	0·2	0·5	0·7

U = Unmanured. M = Manured. M+O = Manure + Oxidizer.

The foregoing observations may be due to either inadequacy of the methods or uneven distribution of the different constituents in the soil. The standard errors of the average values obtained at each stage as also the errors of duplicate determinations of different constituents on individual plots have been given in Tables III and IV and would show that the errors due to analytical methods are very small and do not account for the large variations observed. It may be inferred therefore that the composition of independent specimens taken either from the same area or parallel plots receiving the same treatments are not similar; that there are large variations between parallel samples which account for all the discrepancies observed.

DISCUSSION.

A critical enquiry into the results obtained by many of the previous workers would show that at least some of their conclusions would require modification in the light of certain errors inherent to the methods employed by them. Most of the estimates regarding the changes occurring in the field are based on results obtained with small samples of a few

TABLE II.

Response of individual plots to different treatments.

Treatment	UNMANURED				MANURED								MANURE + OXIDIZER			
Plot numbers	1	2	3	4	1	2	3	4	5	6	7	8	1	2	3	4
Total nitrogen (as p.p.m.) ..	529·8	553·6	548·7	561·1	595·4	574·3	574·9	600·4	530·4	563·1	606·7	578·0	578·2	581·4	553·9	571·6
Std. deviation ± ..	42·6	56·6	34·1	69·9	21·0	55·8	23·5	56·1	108·4	36·8	37·2	59·2	70·8	39·1	84·0	66·5
Ammonia nitrogen (as p.p.m.)	9·6	10·7	10·5	9·9	12·1	12·1	11·6	11·1	12·5	12·2	10·7	11·4	12·3	11·4	14·4	14·1
Std. deviation ± ..	3·2	3·6	2·4	1·3	2·1	1·1	2·4	1·3	2·2	1·7	2·0	2·0	2·8	1·9	1·4	1·5
Nitrate nitrogen (as p.p.m.) ..	4·8	3·9	4·7	4·9	5·2	5·3	4·6	5·0	4·8	6·0	5·1	5·0	4·7	5·5	5·2	5·8
Std. deviation ± ..	0·8	1·6	1·2	1·2	0·8	1·6	1·3	1·0	0·4	1·2	2·6	0·5	1·6	1·7	0·9	0·8
Loss on Ignition (as percentage)	5·1	5·4	5·2	5·4	5·5	5·4	5·5	5·8	5·7	5·5	5·9	5·4	4·9	5·0	5·4	5·2
Std. deviation ± ..	0·5	1·0	0·4	0·4	0·3	0·4	0·5	0·5	1·0	0·5	0·8	0·4	0·7	1·0	0·7	0·8

TABLE III.

Standard error of the average values obtained at each stage.
(32 determinations in each case.)

Form of Nitrogen	Date						
	8-9-1933	18-9-1933	3-10-1933	1-11-1933	1-12-1933	5-1-1934	4-2-1934
Total (as p.p.m.)	4·2	3·9	5·0	4·1	5·2	4·9	6·6
Ammonia (as p.p.m.) ..	0·4	0·2	0·2	0·3	0·5	0·4	0·6
Nitrate (as p.p.m.)	0·3	0·5	0·7	0·5	0·2	0·2	0·6

TABLE IV.

Standard error of the average values for individual plots at each stage.
(14 determinations in each case.)

Treatment →	Unmanured				Manured								Manure+Oxidizer			
Plot number →	1	2	3	4	1	2	3	4	5	6	7	8	1	2	3	4
Form of nitrogen																
Total (as p.p.m.) ..	4·0	6·6	6·3	6·3	5·9	3·7	4·9	3·9	4·2	2·0	4·4	5·7	7·2	7·6	4·7	2·8
Ammonia (as p.p.m.)	0·6	0·3	0·4	0·4	0·7	0·6	0·5	0·3	0·8	0·6	0·5	0·4	0·2	0·3	0·6	0·5
Nitrate (as p.p.m.)	0·3	0·4	0·5	0·6	0·2	0·3	0·8	0·6	0·4	0·4	0·5	0·7	0·6	0·4	0·5	0·4

grams each, so that the related calculations would involve the multiplication of the original errors by hundreds of millions. The influence of certain factors that affect the accuracy of laboratory methods has also to be carefully considered. Thus, it is known that an enhanced nitrogen value can be obtained by merely moistening a specimen of soil (Sreenivasan and Subrahmanyan, *loc. cit.*) so that there will be an apparent increase in nitrogen content if the same specimen is examined just after a shower of rain. Pfeiffer and Blanck (*Landw. Vers. Sta.*, 1913, **78,** 367) considered the analytical error involved in the study of nitrogen balance in the soil and have concluded that the non-homogeneous character of the soil is itself a serious factor which would cause large differences between duplicate determinations or even successive samples. Robinson and Lloyd (*J. Agric. Sci.*, 1915, **7,** 144) have drawn attention to the existence of normal variations in the composition of the soil from point to point in the field. Similar observations have also been recorded by Waynick (*Univ. Calif. Pub. Agric. Sci.*, 1918, **3,** 243) and Waynick and Sharp (*Univ. Calif. Pub. Agric. Sci.*, 1919, **4,** 121) who observed large differences in the total nitrogen, nitrate and carbon contents of field samples of soils. Bear and McClure (*Soil Sci.*, 1920, **9,** 65) and, later, Prince (*Soil Sci.*, 1923, **15,** 395) have shown that the nitrogen contents of specimens of soil and sub-soil chosen from the same plot of land vary in different places and lay emphasis on the error due to sampling in field experiments.

It has been observed by the present authors that even in finely ground and apparently homogeneous specimens of soils, such as are used for analytical work in the laboratory, the distribution of nitrogen is not uniform so that it is not possible to obtain concordant estimates unless the entire specimen is mixed repeatedly and carefully resampled from time to time. It is not surprising therefore to find that independent or even mixed specimens from the same area, however apparently uniform, exhibit striking variations which might be easily mistaken for periodic fluctuations in the composition of the soil. Furthermore, the major part of the nitrogen of the soil is in organic form, being mostly derived from either added manures or plant residues decomposing in it. Since it is not possible in ordinary field practice to distribute the organic matter so evenly as to facilitate accurate sampling for analytical work, it would follow that although the total amounts of nitrogen spread over large areas may be the same, the quantities present in small samples collected as representative specimens may vary considerably. Additional error is also introduced by cattle grazing or sheep-folding during off-seasons, resulting in the droppings being unevenly distributed over the surface of the soil. In assessing the influence of season on processes like nitrogen fixation, the effects of different external factors on the movement of different soil constituents would also require careful consideration. Thus, it is well known that during periods of fallow, a large part of the nitrogen, particularly the soluble forms, moves into the sub-soil and does not become available until the planting of the subsequent crop. During the rainy season, the finer fractions containing the highest percentage of fertilising ingredients would be washed from the surface of a sloping or uneven soil and carried to the lower regions exposing only the less rich, coarse fractions at the surface. Even on the same plot of land considerable variations in the distribution of different soil constituents can be brought about by washing or silting as the case may be.

It would thus be seen that although it is desirable to study changes in the different soil constituents under conditions actually obtaining in field practice, there are yet serious inherent defects due to soil heterogeneity, uneven distribution of matter, erosion and silting so that no accurate estimate of the various changes can be obtained by carrying out studies exclusively on the field. Such investigations are therefore best carried out under the controlled conditions of the laboratory and with uniform specimens of soil, parallel samples of which agree closely in composition.

SUMMARY.

1. The periodic changes in total nitrogen, ammonia, nitrate and organic matter contents of apparently uniform plots of land subjected to different treatments were studied.

2. It was observed that in none of the cases was there any correlation between (*a*) seasonal changes, (*b*) manurial treatment, or (*c*) stage of crop and the variations in the different constituents.

3. Examination of the results obtained in a large number of cases have shown conclusively that the laboratory error due to sampling and methods of analysis is negligible as compared with the field error due to variations in the composition of the soil from point to point. Attention is also drawn to external factors such as erosion, silting and movement of soluble nutrients which lead to uneven distribution of different soil constituents.

4. It is concluded therefore that in the study of biochemical transformation in the soil, experiments conducted with uniform samples and under controlled conditions in the laboratory are likely to yield far more useful results than similar studies conducted on field samples.

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ON THE CHARACTERISATION OF DIFFERENT AMYLASES.

By K. Venkata Giri.

Various methods have been suggested for characterising the different amylases occurring in plants and animals.

Kuhn (*Annalen*, 1925, **444**, 1) differentiated diastatic enzymes into two groups, the α and the β amylases, which attack different points of the starch molecule. Studies on the mutarotation of the sugars formed upon degradation of starch by amylases have led to the discovery that α amylases produce α maltose as the end product whereas the action of β amylases results in the primary formation of β maltose. Kuhn has shown by this method that pancreas and taka-diastase belong to the group of α amylases, while malt amylase can be regarded as a member of the β group. According to Ohlsson and his co-workers (*Compt. rend. Soc. Biol.*, 1922, **87**, 1183; *Compt. rend. Trav. Lab. Carlsberg*, 1926, No. 7, 16; Nordh and Ohlsson, *Z. Physiol. Chem.*, 1931–32, **204**, 89; Ohlsson and Uddenberg, *Ibid.*, 1933, **221**, 165), the dextrinogen amylase (α amylase) and the saccharogen amylase (β amylase) are differentiated by the relative hydrolysis of starch as determined by changes in iodine colouration and reducing action. Waldschmidt-Leitz and Reichel (cited from Willstätter and Rohdewald, *Z. Physiol. Chem.*, 1933, **221**, 13) have developed a method which consists in determining the velocity coefficients of sugar formation and iodine colouration. It has been shown by this method that α amylase of malt and β amylase of barley form 11 and 103 per cents. respectively of maltose from amyloamylose, at which stage the colouration with iodine is negative. This method has been followed by Willstätter and Rohdewald (*loc. cit.*) in their researches on leucocyte amylases wherein they have shown that the amylase is a dextrinase.

The present communication relates to a simple qualitative method of characterisation and differentiation of amylases. In principle the method is based on the observations of Wijsman (*Rec. Trav. Chim.*, 1890, **9**, 1) who was the first to postulate the two enzyme theory of malt amylase in a definite form. He carried out some diffusion experiments with malt amylase and concluded that diastase is a mixture of two enzymes. Later on, several workers have definitely established the existence of the two components of malt amylase. As for the other amylases no definite experimental evidence has so far been adduced to show their plural nature. In the present communication some fresh evidence has been obtained to indicate the plural **nature** of **some** of the amylases investigated.

EXPERIMENTAL.

The method briefly consists in adding a small drop of enzyme solution to a thin layer of agar gel impregnated with starch in a petri-dish and allowing it to diffuse for 28 to 48 hrs. at the laboratory temperature. At the end of the period a dilute solution (N/200) of iodine is poured on the plate, and allowed to remain there for about 2–3 mins., until the colours of all the diffusion zones come out clearly. A deep blue background with a round diffusion field at the centre is formed. The central diffusion field is coloured violet in the case of β amylase and colourless in the case of α amylase. Amylases which contain mixtures of both the components produce a central colourless diffusion field with a violet or green and violet zones surrounding it, depending on the nature of the amylase and starch used.

The substrate medium for the diffusion experiments is prepared as follows: A gel containing 1 per cent. agar-agar together with 0·5 per cent. of soluble starch or 0·2 per cent. of potato starch is prepared. It is then melted and distributed into a number of petri-dishes each of about 4 inches diameter and after the mixture is set, a small drop of the enzyme solution is added to the agar-agar plate, and the diffusion allowed to proceed at the laboratory temperature. Usually, a 24-hour period is chosen for diffusion. If more time is allowed, the diffusion zones become broadened, and clearer and better defined zones are formed.

Figs. I, II and III are reproductions of the diffusion zones obtained for different amylases—(1) Barley malt amylase. (2) β amylase of barley malt (prepared according to Ohlsson's method). (3) Sweet potato amylase (prepared according to the method described by the author (*J. Indian Chem. Soc.*, 1934, **11**, 339). (4) Pancreatic amylase (B. D. H.). (5) Taka-diastase (Parke, Davis & Co.). (6) Salivary amylase.

Figs. I and II show diffusion zones obtained with soluble starch (Zulkowsky's) as substrate, while Fig. III shows the diffusion zones of pancreatic and salivary amylases and taka-diastase with potato starch (B. D. H.) as substrate.

Fig. I is a reproduction of the diffusion zones obtained with malt amylase (*a*), β amylase from malt (*b*) and sweet potato amylase (*c*). It can be seen that sweet potato amylase gives a violet coloured diffusion field similar to that of β malt amylase thereby showing that it is a β or saccharogen amylase. On the other hand, malt amylase which consists of both α and β components gives two diffusion zones, a central one which is colourless and a violet coloured diffusion zone surrounding it.

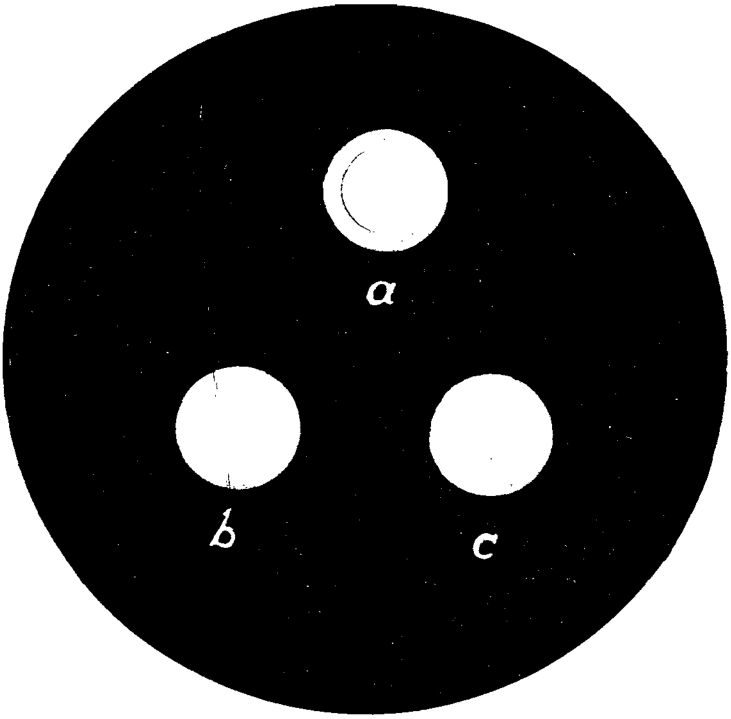

Fig. I.

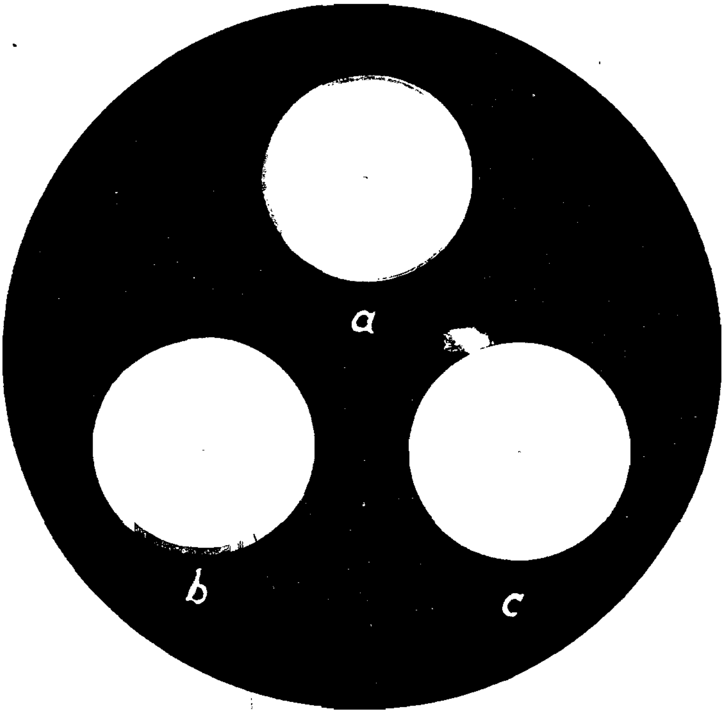

Fig. II.

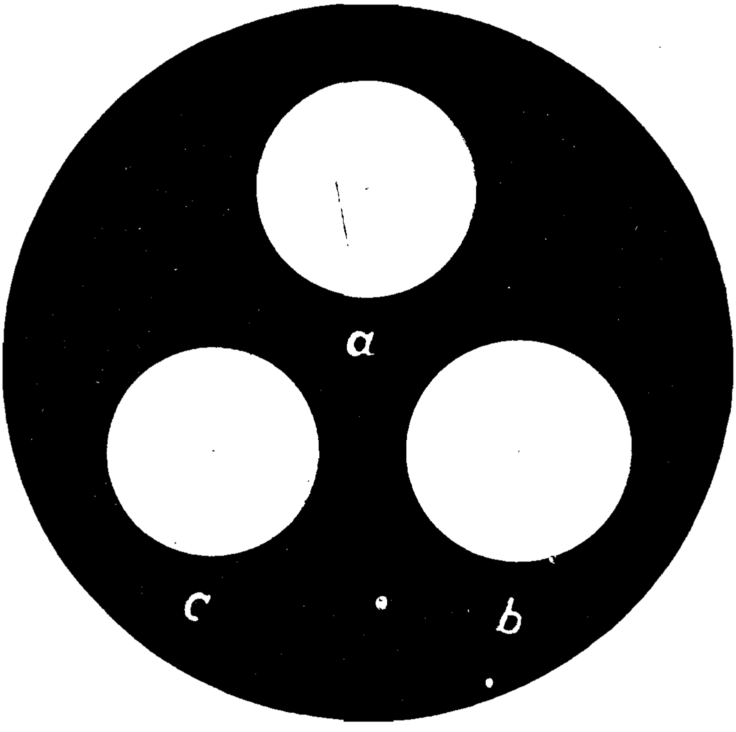

Fig. III.

Thus, amylases containing both components can be easily differentiated from those which contain mainly one component.

Fig. II represents the diffusion zones obtained by salivary amylase (*a*), pancreatic amylase (*b*) and taka-diastase (*c*). Here again there is a distinct difference between the diffusion zones obtained for the three amylases. In the case of taka-diastase there are three distinct diffusion zones—a central, colourless field, a broad green zone, and finally a distinct violet streak surrounding them. In the case of pancreatic amylase, the green coloured zone is narrow compared with that of taka-diastase. With salivary amylase all these characteristics are developed to a far less extent than with the other two enzymes. In all the three cases, however, there appears to be at least two clear diffusion zones, which suggest the presence of two different components.

The differences are more clearly brought out in Fig. III, which reproduces the diffusion zones obtained by the amylases when potato starch is used as substrate. Thus the diffusion zones obtained for taka-diastase are three in number—a colourless central field, a broad, green coloured zone, and finally a very distinct and deep violet coloured ring at the fringe. In the case of pancreatic and salivary amylases, however, only two diffusion zones are formed—a central colourless zone and a green coloured one surrounding it. There is gradation in size and width of the green coloured diffusion zone in all the three cases, taka-diastase producing a broader diffusion zone than pancreatic amylase. In the case of salivary amylase the green coloured diffusion zone is scarcely visible. The three distinct diffusion zones formed by taka-diastase is a characteristic feature indicating the plural nature of this amylase. Attempts to separate the components by physical or chemical methods are in progress.

The author's thanks are due to Prof. V. Subrahmanyan for his keen interest in the work.

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Note.—After the work described in the present paper was completed, there appeared a communication by Giesberger (*Proc. Kon. Akad. Wetensch. Amsterdam*, 1934, **37**, 188) in which the author concludes from diffusion experiments through gelatin that pancreatic and salivary amylases produce diffusion zones which are characteristic of the component nature of the amylases, thereby confirming the observations made independently by the author. The method of Giesberger suffers, however, from the disadvantage that when gelatin is used as diffusion medium, it is liquefied particularly when taka-diastase is used, with the result that all the diffusion zones are not clearly visible—hence the superiority of the present method to that of Giesberger.

CONTRIBUTIONS TO THE STUDY OF SPIKE-DISEASE OF SANDAL (*Santalum Album*, LINN).

PART XVI.—DISTRIBUTION OF ARSENIC IN SANDAL-WOOD TREATED WITH SODIUM ARSENITE.

By A. V. Varadaraja Iyengar.

It was shown in previous communications (Varadaraja Iyengar and Rangaswami, *Indian Forester*, 1934, **60**—under publication) that the spread of spike in an area is considerably checked by killing out diseased plants which act as source of infection and that arsenical tree-killers are highly effective for that purpose. Arising out of this finding, it was considered necessary to know whether any of the applied arsenic passed into the scented heart-wood of the treated plants and, if so, whether the essential oil derived therefrom contained the poison to such an extent as to render it unsafe for use for therapeutic and other purposes. The present enquiry was therefore undertaken to determine the distribution of arsenic in the different parts of the treated plants.

Materials—A number of plants which had been previously treated with known quantities of sodium arsenite (4 lbs. As_2O_3, 1 lb. $NaOH$ in 1 gallon of solution with small amount of added phenol) were pulled out some time after their death and divided into trunk, branches, main root and side roots. Each of these was again further sub-divided into bark, sap-wood and heart-wood. In the case of root-bark especially, adhering soil impurities had to be removed. The final materials were powdered after air-drying and stored. The samples thus obtained were mainly derived from spiked sandal but a few specimens from similarly treated healthy trees were also included for purposes of comparative study.

Methods of Analysis.—The following method was adopted to estimate arsenic:—Known quantities (usually 10 g.) of material were treated with a mixture of nitric and sulphuric acids (10:1) and after the complete cessation of frothing, digested until no trace of carbonaceous matter was left behind. After removing excess of nitric acid, by dilution with water and concentrating repeatedly, arsenic, which was in solution, was determined by different methods, depending on the quantities present. When the quantity was of the order of 50 parts per million and above, it was precipitated as magnesium arsenate (Treadwell and Hall, *Analytical Chemistry*, 1919, Vol. 2). When the quantities were less, it was reduced by zinc and dilute sulphuric acid to arsine, and estimated by the extent of colour produced in standard test papers soaked in mercuric chloride. Both micro and macro methods were adopted for this purpose (Scott, *Standard Methods of Chemical Analysis*, 1927, Vol. I).

The reliability of these methods was checked by adding known quantities of arsenic to different plant materials and verifying the estimates thus obtained. By this means, it was found that the added arsenic could be estimated correct to under 1 per cent. The entire digestion process was carried out in a kjeldahl flask, the acid mixture being added at regular intervals. Addition of hydrogen peroxide (5 per cent.) at periodical intervals was helpful in hastening the decomposition of organic matter. It was found necessary to remove the last traces of nitric acid as also excess of sulphuric acid to obtain accurate estimates of arsenic by colorimetric methods. Incineration of the plant material, with a mixture of equal quantities of sodium and potassium nitrates, was tried without success. Oxidation with perchloric acid was avoided for fear of loss of arsenic as the chloride.

Quantities of solution applied and the efficiency of tree-killer in different girth classes.—For this purpose, the trunk was girdled near the base, to a height of half the girth, the bark removed in this portion and the arsenical solution applied with a brush. The results of the treatments conducted in one of the experimental areas is given in Table I.

TABLE I.

Size in inches ..	2—5	6—9	10—13	14—16	17—20	21—24	25—30
Quantity of solution in ozs. ..	1/16—1/12	1/12—1/10	1/10—1/8	1/8—1/6	1/5	1/4—1/3	1/2
Percentage of death in 5 weeks ..	80	50—60	60—75	50—60	60	80	70

The tree-killer is fairly effective, though the potency can be and has subsequently been improved considerably. The quantity of solution applied bears roughly a direct relation to the size of the plants—the higher girth classes requiring more of the solution.

Distribution of arsenic in the various parts of the treated plants.—The following figures were obtained for the transverse distribution of arsenic in a few representative cases (Table II) :—

TABLE II.

Condition of the plant	Distance from the treated portion in ft.	Arsenic (As_2O_3) as parts per million		
		Bark	Sap-wood	Heart-wood
Spiked	10·0	600	250	60
,	2·0	1,720	1,120	210
,,	0·0 (Treated portion)	No bark	5,960	320
Healthy	0·0 (Treated portion)	do.	8,460	290
,,	2·0	3,490	790	100
,,	3·0	1,610	560	80

It may be seen that the bark contains always a higher proportion of arsenic than the corresponding sap-wood, while the heart-wood contains the least amount. It appears therefore that the spread of the poison is largely through the conducting tracts of the plant.

Vertical gradient of arsenic in the arsenite treated plants.—It has already been shown that the poison travels a considerable distance from the point of application and that in the case of trees which are completely dead, arsenic may be traced even in the smaller roots (Varadaraja Iyengar, *Planters' Chronicle*, 1934, **29**, 240). In the present study further evidence is adduced to show that arsenic moves not only above the treated part along the woody tissues, but also down to the roots chiefly through the bark. The following Table (III) would illustrate the vertical distribution of arsenic in two treated plants which were selected at random and analysed.

TABLE III.

Distance (in ft.) from the point of treatment	Arsenic as As_2O_3 in parts per million			
	Bark		Sap-wood	
	I	II	I	II
Above 15	120	210	70	130
10	470	520	110	220
8	680	760	230	350
5	820	1,090	360	490
3	940	1,420	420	680
2	1,080	2,150	750	960
1	2,840	3,430	1,040	1,650
Treated part, *i.e.*, zero	No bark	No bark	4,180	5,610
Below 6 in.	2,480	2,810	1,450	2,280
12 in.	1,725	2,180	1,080	1,550
1 ft. 6 in.	1,320	1,860	640	1,010
3 ft.	840	1,270	460	790
4 ft.	160	980	120	530

In the case of underground parts, big side roots were selected for study, in view of the difficulty of collecting all the roots of the plants at a given depth. This procedure was further justified by the fact that sandal is largely a surface feeder.

In the immediate vicinity of the treated portion, the tendency of arsenic movement would be more downward than upward. It is clear that the gradient recorded is not strictly proportional to the distance from the point of application. It is of interest to observe that shortly after application of the poison, the leaves turn flaccid, developing a characteristic brown colour. Moreover, the external symptoms of death in the foliage and at the growing points resemble the wilting condition consequent on insufficient water supply. It is probable that the effect of the poison is localised in the treated part, the water conduction being inhibited.

It may further be noted that thin roots (less than 2″ in thickness) contained only traces of arsenic. It has also been found that in a number of cases, arsenic had travelled to root-suckers of the treated parent plants and killed them. It would appear in these cases, that the poison had moved farther through some roots than others.

Arsenic in the scented-wood and oil.—Examination of a number of specimens of heart-wood from treated plants showed that all of them contained arsenic though in minute quantities. The results are presented in Table IV.

TABLE IV.

Specimen Number and Condition of Sandal	Arsenic as As_2O_3 in p.p.m.	Specimen Number and Condition of Sandal	Arsenic as As_2O_3 in p.p.m.
1 spiked	320	7 spiked	40
2 ,,	180	8 ,,	180
3 ,,	210	9 ,,	160
4 ,,	100	10 healthy	210
5 ,,	290	11 ,,	350
6 ,,	80	12 ,,	270

Although the quantities of arsenic passing into the heart-wood are very small, it still appeared probable that traces of the poison may pass into the oil and thus affect its quality. With a view to verifying this, samples of the wood were powdered to pass the 40-mesh sieve and the oil extracted by both the solvent and the steam distillation methods. In the former case, the method of Briggs (*Ind. and Eng. Chem.*, 1916, **8**, 428) was adopted. In the latter, the oil was distilled with steam at a pressure of 25-30 lbs. for nearly 5 hours. The specimens of oil obtained by both the methods were digested with acid mixture and the arsenic in the digest estimated in the manner already described. Careful examination of a dozen samples showed, however, that not even a trace of the poison was present in any of them. The reliability of this conclusion was tested independently as follows: Experiments with known quantities of arsenic added to the oil under study showed that the same could be estimated correct to under 1 per cent. These observations show conclusively that, in spite of the presence of arsenic in the heart-wood of the treated plants, none of it passes into the oil derived from it.

It became of interest, however, to know whether arsenic comes at all during distillation with steam. To this end, the distillate after the separation of the oil was concentrated to a small volume and digested with acid mixture and arsenic estimated in the extract. It was found that a small quantity of the poison does pass over, the amount varying from 7 p.p.m. to 20 p.p.m. In a few instances, no trace of this constituent could be detected (Varadaraja Iyengar, *Half-Yearly Reports on Spike Disease of Sandal*, Pt. VII, 1933). The reason for the presence of arsenic in the distillate lies probably in the possible transfer of fine particles of the scented wood with steam. There is, however, no indication that oxides of arsenic are steam volatile. It follows therefore that all the arsenic is in the residue only. Moreover, the water is discarded in the process of collecting the oil. It may further be pointed out that the only possible manner in which the poisonous element can enter into the composition of the oil is through the formation of organic derivatives of arsenic. The analyses conclusively prove that such derivatives are not formed. Thus the quality of the oil is not impaired, in any manner.

Transmission of the poison to root-suckers.—In the course of some experiments conducted in N. Salem forest areas, it was observed that in addition to treated plants some untreated ones also showed signs of arsenic poisoning and died. A careful examination of the roots of the latter, revealed that they were suckers originating from the treated ones, showing thereby that the poison may have been transmitted to them through the connecting roots. Since this observation is of great practical interest, the roots of the treated plants, as also those of the suckers, were examined for their arsenic contents (Table V). In both cases the root specimens were derived 2-3 ft. below ground, at a distance of 5 ft. from the respective plants.

TABLE V.

Arsenic as As_2O_3 in p.p.m. in the roots of

Treated Plants		Root-suckers	
Bark	Sap-wood	Bark	Sap-wood
480	230	180	60
610	340	240	80
560	240	170	50

DISCUSSION.

The mechanism of death in plants resulting from arsenic poisoning has not been adequately studied. When arsenic as arsenate is added in minute quantities to the soil, an increase in growth of plants is generally noticed. In larger amounts the plants die preceded by intense withering of the foliage. Among the various arsenic compounds, sodium arsenite is the most potent, acting even in concentrations of 1 : 250,000,000. It would appear that the poisonous action proceeds from the roots, in which the protoplasm is disorganised, hindering osmotic action, resulting in the final death of the roots. According to Mathieu (*Ann. Falsif.*, 1912, **5**, 78) more arsenic is detected in grapes and wine from vines sprayed with arsenicals than from untreated ones, thereby indicating the translocation of the poison to different parts. A more descriptive account on the subject is presented by Brenchley (*Inorganic Plant Poisons and Stimulants*, 1927). Recently Crafts and Kennedy have studied the conditions that determine the effectiveness of chemicals in weed control (*Plant Physiol.*, 1927, **2**, 503). In a later contribution, these authors (*ibid.*, 1930, **5**, 329) followed the course of arsenic when applied to the leaves of *Convolvulus arvensis* (Morning-glory). They have found the presence of arsenic even in the distant roots, though only in small amounts. It is well known that the effectiveness of a plant poison is dependent upon penetration and subsequent distribution in the several tissues. These factors are more important when the destruction of diseased tissues which act as source of infection is concerned. In the case of arsenic, penetration is best effected by the incorporation of acids or bases which hasten diffusion of the poison. But the distribution of the poison is influenced by the mode of application, the strength or potency of the chemical and finally, by the physiological condition of the plant.

In the present study, the plants were girdled, the bark removed to expose the woody portion, and the solution smeared on it. By this means it was hoped that the poison would reach both the foliage and the roots acting on its way. Mere girdling of the plant to expose the wood, does not result in its death, while in presence of the toxic material, the aerial parts die quickly. The manner in which this is brought about will be considered here. An examination of Table III will show that both the sap-wood and bark of either stem or root, contain large quantities of arsenic, while the heart-wood contains far less amount (Table II). Moreover, a gradient in arsenic content is visible though it is not strictly proportional to the distance from the region of treatment. Two possibilities may be considered in explaining the mode of transfer of arsenic. Primarily, the poison applied at the exposed woody part moves along the transpiration stream and traverses down the bark with the organic nutrients from the leaves.

The accumulation near the 'ring' may then be due to discontinuity of the bark. Alternately, it is possible that above the girdle, arsenic is transferred to the bark as it moves along the transpiration stream. This may explain the progressively decreasing concentration of arsenic in the distant aerial parts. Arsenic has also been detected in the leaves, but no excessive accumulation has been noticed. Of the two theories regarding the movement of arsenic, the latter one seems more plausible when considering that with the progress of disease, accumulation of starch takes place in stem and leaves inhibiting the movement of food materials. Experiments with cut shoots in dilute solutions of sodium arsenite have failed to show the presence of arsenic in the bark. Below the girdle, however, arsenic movement has not been very rapid. A great accumulation has been noticed near the girdled part, while the distant roots do not have much arsenic in them. The defective translocation, so characteristic of spike, is perhaps responsible for this. The conditions that determine the penetration and distribution of arsenic below the 'ring' are still obscure. A critical analysis of the various factors will form the theme of a later contribution.

It is significant to find that in all the cases examined the concentration of arsenic is greatest in the bark, less in the sap-wood and least in the heart-wood (Tables III and IV). These observations show that the poison travels or is present in considerable quantities only in the conducting tracts of the growing plant. The extremely low value in the scented wood is due to the fact that it is a dead tissue and as such, transfer of the poison therein is rather poor. On the other hand, a lateral diffusion to the bark tissue is possible in view of the nearness to the woody portion and the large amount of alkali in the solution applied.

It is well known that root-suckers from spiked sandal are generally diseased, thus acting as source of infection. The penetration of the poison even to the suckers shows its high efficiency in killing out diseased material. The amount of poison in them is, however, far less than that of the parent plants (Table V).

Although the poison penetrates rapidly into the bark tissue, it is low in amount in the heart-wood. The complete absence of arsenic in the oil derived from the treated trees, establishes convincingly that the adoption of arsenical tree-killers does not in any way affect the use of the oil for therapeutic and other purposes.

SUMMARY AND CONCLUSIONS.

1. In arsenical treated spiked sandal plants, large quantities of the poison are found to be present in the bark and sap-wood.

2. Movement of the poison has been noticed even in the roots at some distance from the point of application.

3. The greatest concentration of arsenic is found near the girdled region.

4. Root-suckers of treated plants are also often killed out, due to transfer of the poison to their roots.

5. In spite of the presence of minute quantities of arsenic in the heart-wood of treated plants, the oil derived from them does not contain any of the poison, irrespective of the method of extraction. The application of arsenicals for control of spike-disease is thus free from objections.

6. The mechanism of death due to arsenic application appears to be due to effective penetration and thorough distribution of the same immediately above, in and below the girdled portion, killing the tissues and thus inhibiting nutrient supply.

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THE ESTIMATION OF CHLORINE IN WATER BY THE *o*-TOLIDINE METHOD.

By S. D. Sunawala and K. R. Krishnaswami.

The practice of chlorinating the water supplies of large towns is fast becoming almost universal. On account of the harmful effects of chlorine on the human system and its bleaching action on coloured fabrics, it is very desirable to have a reliable method for the accurate estimation of the small quantities of free chlorine usually present in chlorinated water supplies.

Of the various methods which have been suggested from time to time the best known is the *o*-tolidine method which depends on the yellow coloration produced by the addition of *o*-tolidine to a solution containing free chlorine. This method was developed by Ellms and Hauser (*J. Ind. Eng. Chem.*, 1913, **5**, 915; 1914, **6**, 553) and was subsequently adopted by the American Public Health Association in their standard methods for water analysis. Considerable work has been done concerning the sensitivity of the method as well as its applicability under different conditions. Ellms and Hauser reported that the method yielded positive tests with chlorine up to a minimum concentration of 0·005 part per million (p.p.m.) in aqueous solution, and that there was a gradation of colour with increasing concentrations of chlorine. They proposed a set of permanent colour standards for comparison by the use of solutions of potassium dichromate and copper sulphate of various concentrations. Further, they found that the presence of iron salts or nitrites in the sample of water to be tested did not interfere with the accuracy of the chlorine test unless they were present in rather unusual quantities, namely, to the extent of more than about 1 p.p.m. and 0·09 p.p.m. respectively. Buswell and Boruff (*J. Amer. Waterworks Assoc.*, 1925, **14**, 384; *Br. Chem. Abstr.*, 1926, **B**, 174) confirmed the results of Ellms and Hauser and obtained accurate results in the estimation of chlorine in concentrations 0·02—0·2 p.p.m. by employing the permanent colour standards suggested by the latter authors. Hopkins (*J. Ind. Eng. Chem.*, 1927, **19**, 744) found that although stable salts of manganese like the chloride or the sulphate did not interfere with the estimation of chlorine by the *o*-tolidine method, the presence of permanganate or manganous hydroxide even in very small concentrations rendered the method quite unsuitable. McCrumb (*J. New England Water Works Assoc.*, 1927, **41**, 386; *Br. Chem. Abstr.*, 1928, **B**, 38) emphasised the need for maintaining a pH value of 2 or less in the solution under test because the colour producing substance was a H° indicator giving the desired yellow colour only when the acidity of the solution corresponded to that value. He also devised a comparator set with the help of which he claimed that it was possible to avoid interference due to turbidity and the presence of salts of iron, manganese and nitrites in the sample. Anselmi and Calo (*Annali. Chim. Appl.*, 1930, **20**, 410; *Br. Chem. Abstr.*, 1930, **B**, 1170) investigated several methods for the estimation of chlorine and found the *o*-tolidine method to be the most satisfactory. They recommended its use in estimating quantities ranging from 0·02 to 0·2 p.p.m. and the starch iodide method for higher concentrations. McCrumb and Kenny (*J. New England Water Works Assoc.*, 1928, **42**, 410; *Br. Chem. Abstr.*, 1929, **B**, 114) investigated the development and fading of the colour in samples exposed to direct sunlight and found that the results obtained were unreliable unless the sample was kept protected from sunlight in brown bottles. Hanal and Jaffè (*Analyst*, 1932, **57**, 308) noticed the interference of nitrites in the estimation of chlorine by this method and suggested that it should be applied only after ensuring the absence of nitrites by a preliminary test with *m*-phenylenediamine hydrochloride.

The method of testing employed by all the above workers was on the lines originally suggested by Ellms and Hauser (*loc. cit.*), which consist in the addition of 1 c.c. of *o*-tolidine reagent (1 g. in 1 litre of dilute HCl) to 100 c.c. of the sample under examination. A yellow colour is produced if free chlorine is present in the sample and since this colour deepens gradually for about 3 minutes, and then remains unchanged for about 30 minutes, it is matched after the expiry of 5 minutes with the colours given by solutions containing known quantities of chlorine or with the specified potassium dichromate standards. It appears from the preceding account that the estimation of chlorine especially in low concentrations is attended with uncertainties due to (*a*) interfering substances such as salts of iron and manganese and nitrites, (*b*) time required for colour to attain maximum intensity, (*c*) fading of the colour after a certain period, and (*d*) effect of sunlight as well as temperature on the rate of development of colour. This investigation was undertaken with a view to obtain additional data regarding the nature and extent of interference from the above sources and to devise a procedure by following which reasonably accurate results could be obtained.

EXPERIMENTAL.

Preparation of Materials.—The chlorine required for preparing the solutions for estimation was obtained from a steel cylinder containing liquid chlorine.

The pure water employed for the preparation of solutions of chlorine was of the conductivity grade and was obtained by distillation from an alkaline permanganate solution, an all-glass apparatus with a silica condenser being employed for the purpose.

The *o*-tolidine reagent was prepared in the manner recommended by Boruff (*J. Amer. Waterworks Assoc.*, 1928, **20**, 401 ; *Br. Chem. Abstr.*, 1928, **B**, 246) by dissolving 1 g. of *o*-tolidine in 1 litre of dilute (7·5 p.c.) hydrochloric acid and by using it, 0·01 p.p.m. of chlorine could be detected with certainty.

Solutions with low concentrations of chlorine, *viz.*, less than 1 p.p.m. were always freshly prepared by diluting a stronger solution which had been accurately standardised iodimetrically by titration with sodium thiosulphate using starch as indicator. Comparison of intensities of colour could be performed when the solutions were kept in Nessler jars, but most of the data obtained in this work were obtained with the help of a simple type of colorimeter.

Rate of development and fading of the colour and influence of temperature on same.—To 100 c.c. of a sample of water containing 0·2 p.p.m. of chlorine kept in a Nessler jar, 1 c.c. of *o*-tolidine reagent was added and the liquid agitated by a glass stirrer. Part of the liquid was then transferred to the colorimeter tube which had a tap at the side to facilitate withdrawal of small quantities of the solution, and matched against the permanent standard solution (0·2 p.p.m) kept in the other tube at a constant level. The matching was done at regular intervals from the start by noting the height of the column of the test solution required to produce the same colour intensity as the standard, this being done by either withdrawing a part of the liquid from the tube or adding some more of the test solution from the Nessler jar. Duplicate readings usually agreed to within 2 m.m. but since three or four readings were obtained for each setting and at least two experiments were always performed, the accuracy of the measurements was considered to be sufficient for our purpose.

The results obtained in two sets of experiments carried out at 20° and 30° respectively are shown in Table I as well as in Fig. 1.

TABLE I.

Time minutes	Standard cm. (h_0)	Test cm. (h_1)	Colour intensity $1/h_1$	h_0/h_1	Temp.
2	14.0	16·0	0·063	0·88	30
3	,,	15·0	0·067	0·93	30
5	,,	14·5	0·069	0·97	30
5	,,	17·3	0·058	0·81	20
10	,,	14·2	0·070	0·99	30
10	,,	15·9	0·063	0·88	20
15	,,	14·2	0·070	0·99	30
20	,,	14·2	0·070	0·99	30
20	,,	14·9	0·067	0·94	20
25	,,	14·2	0·070	0·99	30
30	,,	14·2	0·070	0·99	20
35	,,	14·5	0·069	0·97	30
45	,,	15·0	0·067	0·93	30
45	,,	14·2	0·070	0·99	20
60	,,	15·5	0·064	0·90	30
60	,,	14·5	0·069	0·97	20
75	,,	17·1	0·059	0·82	30
90	,,	18·4	0·055	0·76	30
90	,,	15·6	0·064	0·88	20
120	,,	21·3	0·047	0·66	30
120	,,	17·8	0·056	0·79	20
150	,,	24·7	0·040	0·57	30
150	,,	20·4	0·049	0·69	20

The results given in the above table and the curves in Fig. 1 indicate that a certain period of time elapses before the colour reaches

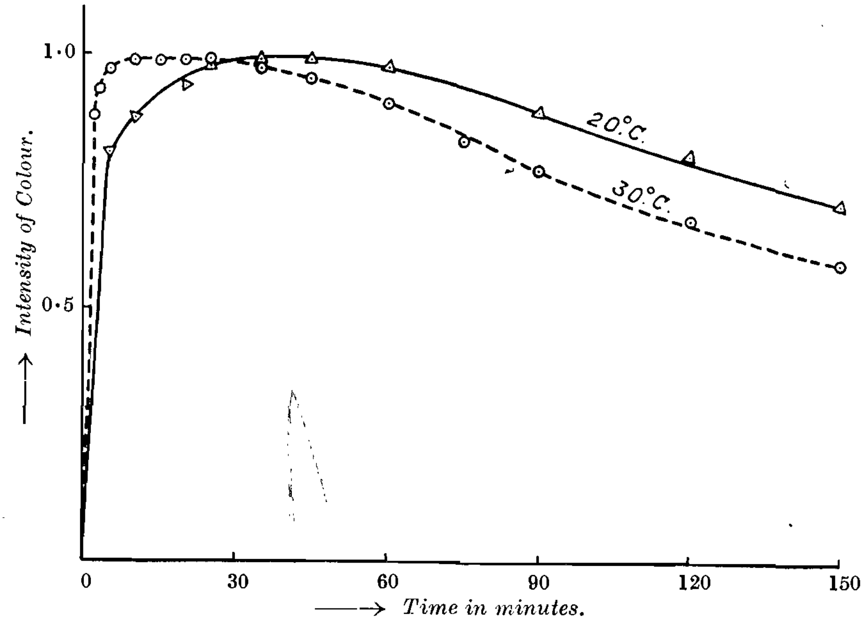

Fig. 1.

Development and Fading of Colour with Chlorine (0·2 p.p.m.) at 20°C. and 30°C.

its maximum intensity at which it remains steady for about 15 minutes and then begins to fade gradually. Further, it is apparent that the colour attains maximum intensity much more quickly at 30° than at 20° and that the fading process sets in at different intervals. It appears therefore necessary that whereas in experiments carried out at 20° the comparison should be made after about 30 minutes but within 45 minutes, in those at 30°, it should be done earlier, *viz.*, between 10 and 25 minutes. These conditions were adhered to in all our subsequent determinations.

Proportionality between colour intensity and chlorine concentration.—Samples of water containing 0·1, 0·2,....up to 1·0 p.p.m. of chlorine in water were prepared in the manner mentioned earlier and the colours developed on the addition of *o*-tolidine to the various samples were matched in the colorimeter with dichromate solutions which according to the tables of Ellms and Hauser (*loc. cit.*) were equivalent to 0·2, 0·5 and 0·8 p.p.m. of chlorine. The three different colour standards mentioned above were taken in order that the colours compared might in every case be of the same order of intensity, as otherwise the matching operation would be inconvenient. The results obtained are shown in Table II and also in Fig. 2.

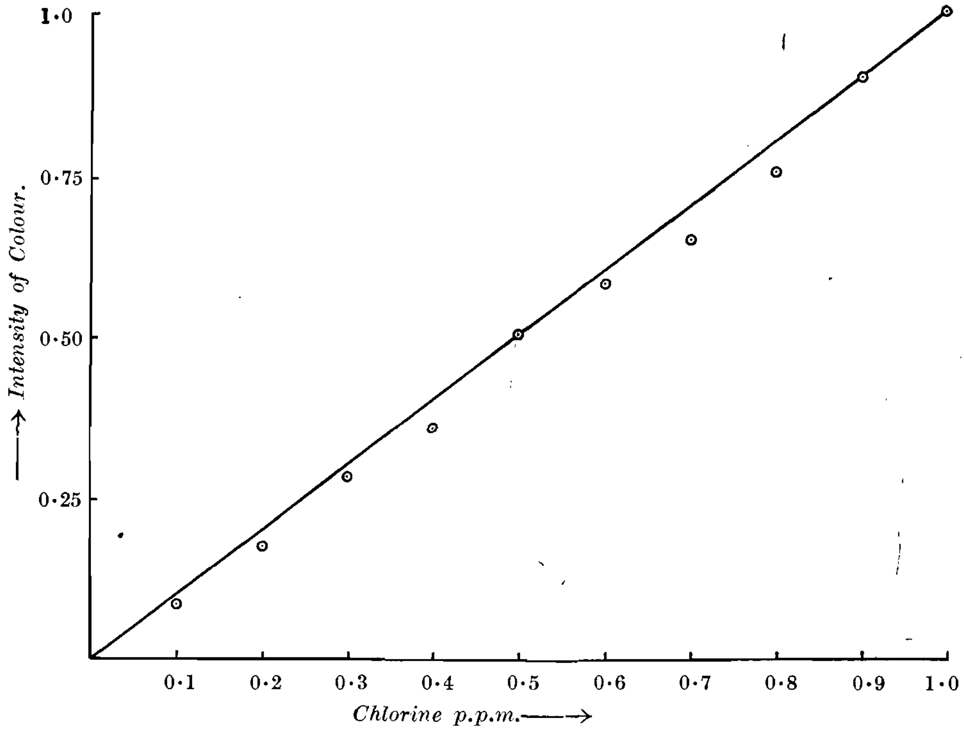

Fig. 2.

Variation of Intensity of Colour with strength of Chlorine Solution.

TABLE II.

Permanent standard p.p.m.	Height of standard cm.	Chlorine p.p.m.									
		0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
		Height of solution in cm.									
0·2	11·0	22·0	11·0	6·9	..	..	..	..	..	..	..
0·5	6·7	..	..	11·7	9·4	6·5	5·6	..	..	..	..
0·8	7·0	..	..	..	..	..	9·1	7·9	6·9	5·9	5·1

The results given in the above table might be recalculated in order to express all the heights with reference to that of 0·2 p.p.m. solution, *viz.*, 11·0 cm., and the figures so obtained are given below in Table III.

TABLE III.

Chlorine p.p.m.	Height in matching tube h	Colour intensity $1/h$	$(1/h)/0{\cdot}527$
0·1	22·0	0·045	0·09
0·2	11·0	0·091	0·17
0·3	6·9	0·145	0·28
0·4	5·55	0·182	0·35
0·5	3·85	0·263	0·50
0·6	3·3	0·303	0·58
0·7	2·9	0·345	0·65
0·8	2·5	0·400	0·76
0·9	2·15	0·476	0·90
1·0	1·985	0·527	1·00

It is seen from Table III and more clearly from Fig. 2 that the intensities of colour developed in solutions of chlorine are roughly proportional to their chlorine concentration in the range studied.

The reliability of the method in presence of salts of iron and manganese and nitrites.—The reliability of the *o*-tolidine method in presence of ferric salts was investigated as follows: Several lots of chlorine water of known concentration (0·2 p.p.m.) were freshly prepared and to these were added a standard solution of ferric sulphate in such quantities that chlorine solutions (0·2 p.p.m.) containing various known quantities of iron up to 3·3 p.p.m. were obtained. *o*-Tolidine reagent was added to these solutions and the colorimetric comparison made with the permanent standard solution (0·2 p.p.m.) at definite intervals for a period of 2½ hours. The results obtained are shown in Table IV and also in Fig. 3.

TABLE IV.

Chlorine solution employed: 0·2 p.p.m.

Time minutes	Fe (p.p.m.)				
	0·0	0·28	0·56	1·40	2·80
	Intensity of colour				
2	0·88	0·90	0·69	0·75	0·84
3	0·93	..	..	..	0·96
5	0·97	0·95	0·81	0·92	1·07
7	..	..	..	0·96	..
8	..	..	..	..	1·24
10	0·99	0·98	0·89	1·07	1·40
15	0·99	1·00	0·96	1·20	1·70
20	0·99	..	..	1·36	2·09
25	0·99	1·00	1·05	1·52	2·50
30	..	..	..	1·69	..
35	0·97	..	..	..	2·74
40	..	1·00	1·12	..	..
45	0·93	..	..	2·09	3·04
1 hr.	0·90	0·91	1·12	2·30	3·18
1¼ ,,	0·82	..	1·06	..	..
1½ ,,	0·76	0·84	0·99	2·75	3·42
2 ,,	0·66	0·69	0·84	..	..
2½ ,,	0·57	0·49	..	..	..

The figures given in the above table and the curves in Fig. 3 clearly indicate that the results obtained are accurate only if iron is present in quantities not exceeding 0·28 p.p.m. while larger quantities of iron interfere in the determinations and the results obtained by comparison at the stage of maximum colour intensity are abnormally high. This

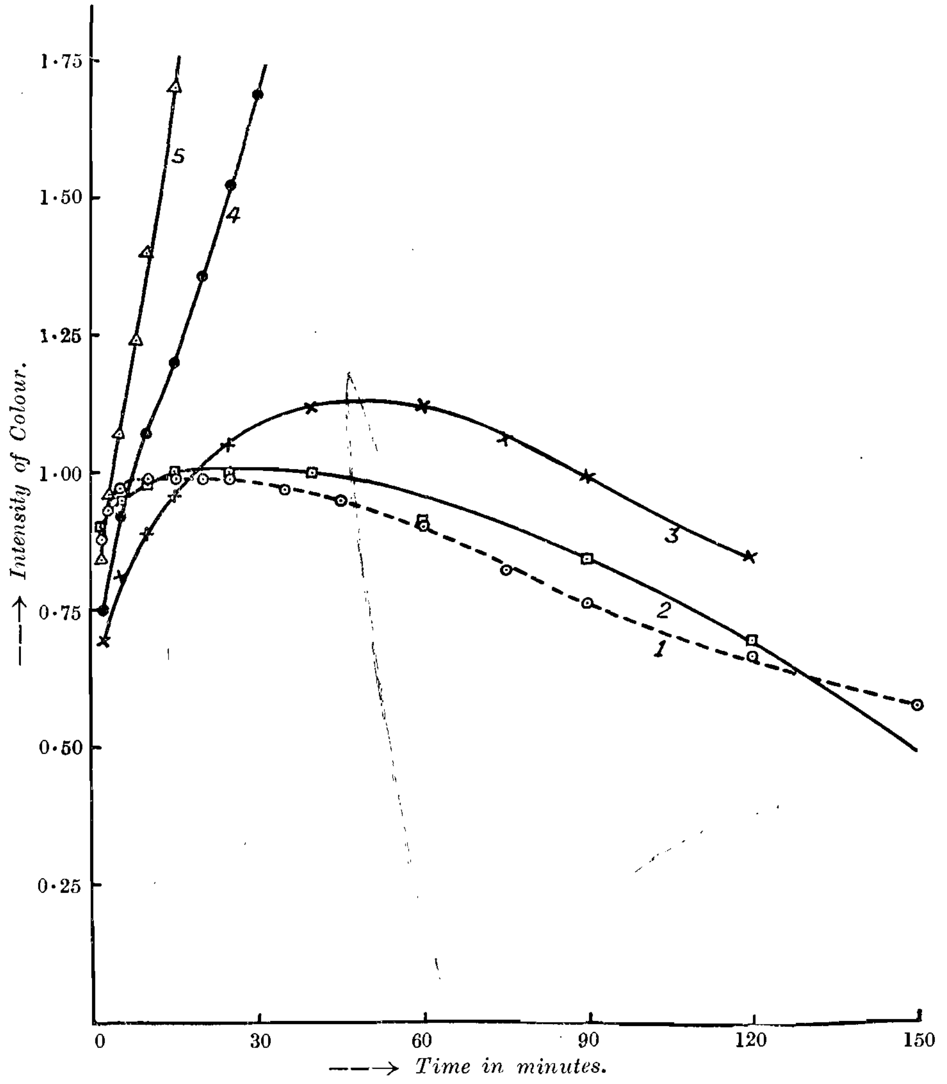

Fig. 3.

The Influence of Iron on the Estimation of Chlorine.

1—Chlorine (0·2 p.p.m.)
2— do. do. + Iron (0·28 p.p.m.)
3— do. do. + do. (0·56 do.)
4— do. do. + do. (1·40 do.)
5— do. do. + do. (2·80 do.)

at variance with the observation of Ellms and Hauser (*loc. cit.*) hat correct results could be obtained in presence of iron up to a aximum concentration of 1 p.p.m.

The next point to be investigated was whether the high values obtained in presence of iron could be corrected for, if the iron content of the solution was known and also the colour intensity which that quantity of iron would produce with *o*-tolidine in water entirely free from chlorine. This was done as follows:—To several lots of distilled water contained in Nessler jars was added a standard solution of ferric sulphate in such quantities that solutions containing respectively 0·28, 0·56, 1·40 and 2·80 p.p.m. of iron were obtained. To these solutions *o*-tolidine was added and the coloration developed was matched against a permanent colour standard. The results obtained are shown in Table V.

TABLE V.

Time minutes	Fe (p.p.m.)			
	0·28	0·56	1·40	2·80
	Intensity of colour			
10	..	..	..	0·19
15	..	..	0·15	0·35
20	..	..	0·22	..
25	..	..	0·30	0·57
30	..	..	0·36	0·77
45	..	0·23	0·67	1·22
60	..	..	1·00	1·71
75	..	0·37	1·31	..
90	0·20	..	1·49	2·60
105	..	0·51	1·73	..
120	0·25	..	..	3·11
135	..	0·63	2·03	..
150	0·29	0·68	2·03	3·11
180	0·28	..	..	2·98
210	..	0·58	1·61	..
240	0·24	..	..	2·59

The results given in Table V indicate that a coloration is produced on the addition of *o*-tolidine to water containing iron even in such small concentrations as 0·28 p.p.m. although a considerable period elapses before it is noticeable. With higher concentrations of iron the development of colour is more rapid.

A few experiments carried out on the same lines as mentioned above showed conclusively that manganese sulphate, even when present in high concentrations (100—1000 p.p.m.) did not interfere with the accuracy of the chlorine determination.

The extent to which nitrites interfere was ascertained by carrying out a few experiments in which small quantities of nitrites were added to a chlorine solution of known concentration (0·2 p.p.m.). The colour produced by *o*-tolidine in presence of nitrites was brownish and could not be matched with the dichromate standards. This point was not investigated further because it was evident that even small concentrations of nitrites rendered the estimation difficult.

SUMMARY.

The following points have been elucidated from a study of the *o*-tolidine method for the estimation of chlorine :—

(1) The colour developed on the addition of *o*-tolidine to solutions of chlorine in water takes an appreciable time to attain maximum intensity at which it remains steady for some time, and then fades gradually, the rates of the two processes depending on the temperature of the solution.

(2) The most suitable time for making the comparison of colour intensities depends on the temperature and is between 10–25 minutes at 30° and 30–45 minutes at 20°.

(3) The presence of ferric ion in solution yields high results except when it is present in concentrations of less than about 0·3 p.p.m. Attempts to devise a correction factor for this interference were unsuccessful.

(4) The method is inapplicable to samples containing nitrites even in low concentrations.

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CONTRIBUTIONS TO THE STUDY OF SPIKE-DISEASE OF SANDAL (*Santalum Album*, LINN).

PART XVII.—HYDROGEN-ION CONCENTRATION AND BUFFERING CAPACITY AS FACTORS OF DISEASE RESISTANCE.

By M. Srinivasan and M. Sreenivasaya.

Disease resistance in plants is a problem of great economic value since it offers the most rational and effective method of combating the diseases affecting them. The factors imparting disease resistance are both mechanical and physiological. Cuticular structure of the host (Valleau, W. D., *J. Agr. Res.*, 1915, **5**, 365; Willamann, J. J., Pervier N. C., and Triebold, H. O., *Bot. Gaz.*, 1925, **80**, 121; Lutman, B. F., *Vt. Agr. Exp. Sta. Bull.*, 1919, 215), waxy coatings (Howitt, J. E., *Rept. Que. Soc. Prot. Plants*, 1924, **16**, 9) and hairy growth of the epidermis (Blackmann, V. H., *B.A.A.S.*, 1924, Sec. K, 1-14) are some of the known types of defensive mechanism.

When the host is infected despite the mechanical barriers, physiological factors of resistance come into play. Among such factors may be mentioned a highly toxic or agglutinating medium obtaining in the host (Berridge, E. M., *Ann. Appl. Biol.*, 1929, **16**, 567) and the presence therein of tannins (Cook, M. T., and Taubenhaus, J. J., *Delaware Agr. Exp. Sta. Bull.*, 1911, 91; Cook, M. T., and Wilson, G. W., *N. J. Agr. Exp. Sta. Bull.*, 1916, 291; Graves, A. H., *Phytopath.*, 1926, **16**, 615; Hawley, L. F., Fleck, L. C., and Richards, C. A., *Ind. Eng. Chem.*, 1924, **16**, 699), alkaloids and glucosides (Reynolds, E. S., *Plant Physiol.*, 1926, **1**, 151; Brierley, W. B., *Rept. Internat. Potato Confer.*, London, 1921, 93), phenols (Newton, R., and Anderson, J. A., *Canadian J. Res.*, 1929, **1**, 86) and sulphur compounds (Tims, E. C., *J. Agr. Res.*, 1926, **32**, 183), all of which have been shown to exert an inhibitory influence on the growth of parasites.

Free hydrogen ions in the cell sap of the host as a determining factor in disease resistance is a recent idea. So far, no correlation between them has been recorded (Hawkins, L. A., and Harvey, R. B., *J. Agr. Res.*, 1919, **18**, 275; Weiss, F., and Harvey, R. B., *J. Agr. Res.*, 1921, **21**, 589; Hurd, A. M., *J. Agr. Res.*, 1923, **23**, 373; *ibid.*, 1924, **27**, 725; Hurd-Karrer, A. M., *Amer. J. Bot.*, 1925, **12**, 359; Mumford, E. P., *Ann. Appl. Biol.*, 1930, **17**, 28; Newton, R., Lehmann, J. V., and Clarke, A. E., *Canadian J. Res.*, 1929, **1**, 5), though Comes (*Reale Istituto d' Incoraggiamento di Napoli*, 1916, 1; *Bull. Agr., Intelligence*, **7**, 1205) argued that acidity was a very important factor determining immunity in plants. Laurent (*Ann. de l'Inst. Pasteur*, 1899, **13**, 1) and Lepoutre (*Ann. de l'Inst. Pasteur*, 1902, **16**, 304) observed that reduction in the acidity of the cell sap did in some way facilitate the attack of bacteria on plant tissues. However, all these authors only tried to correlate disease resistance with initial acidity of the host tissue fluid, but not with its buffering capacity. Only one attempt till now seems to have been made in this direction without definite conclusions (Wille, F., *Zentr. Bakt., Abt. II*, 1933, **87**, 340).

In the course of our investigations on sandal, we observed that sandal growing in combination with certain species of host plants withstood the attack of spike-disease even through grafting (*Investigations on the Spike-Disease of Sandal—Working Committee Report*, 3, 1931). That immunity in sandal is largely controlled by associated host plants even under sylvicultural conditions has been shown by Sreenivasaya and Rangaswami (*J. Indian Inst. Sci.*, 1931, **14A**, 59).

The present communication is a study of hydrogen-ion concentration and buffering capacities of the tissue fluids of sandal in their relation to disease resistance. For this purpose, sandal plants in combination with *Ruta graveolens*, *Murraya kœnigii*, *Melia azadirachta* and *Toddalia aculeata*—types of hosts imparting resistance—and those in combination with *Acacia farnesiana*,—a type rendering sandal susceptible to disease—have been studied, together with spiked plants and those growing without a host.

EXPERIMENTAL.

Sandal plants for the investigation were reared as follows:—Seedlings were transplanted into pots containing suitable make-up of soil and manure, as also the desired host plants. In one instance no host was supplied. The plants were watered daily. For receiving fresh supplies of manure, the growing plants along with their hosts were transplanted into bigger pots from where they were removed at the desired stages for experimental purposes. Together with healthy sandal, spiked ones of the same age and feeding on the same hosts (*Acacia farnesiana*) as the healthy were selected. By thus choosing plants of the same age and grown under equal environmental conditions, inherent differences, due to host combinations or disease, would not be masked in respect of initial acidity and buffering capacity.

For the experiments, the plants were pulled out of the pots, adhering soil washed off in running tap water, then with distilled water and dried by pressing between folds of filter paper. They were then divided into (1) leaf, (2) bark, (3) wood and (4) root.

The samples, collected at 9 A.M. each day, were treated with toluene (after shredding in case of wood and root), in wide-mouthed bottles, stoppered and left in ice-room. After 24 hrs., sap was expressed from the tissues as described previously (Sreenivasaya, M., and Sastri, B. N., *J. Indian Inst. Sci.*, 1928, **11A,** 23; *ibid.*, 1929, **12A,** 239). The saps obtained with root and wood tissues were so small that centrifuging was not possible, so these, as well as the other experimental tissue fluids, were all filtered prior to electrometric titrations. Filtering does not detract from the accuracy of the results, for Harvey (*J. Biol. Chem.*, 1920, **42,** 397) showed that in a buffered plant juice, minor differences in concentration did not affect hydrogen-ion measurements appreciably. Hurd (*loc. cit.*) did not centrifuge the sap in her experiments on varietal disease of wheat rust, but strained it through cloth. Similarly, Martin (*Protoplasma*, 1928, **3,** 273) used filtering as a method of clarifying saps in her study of the buffers of sun-flower stem and root, while Haas (*Soil Science*, 1920, **9,** 341) in determining acidity and buffering capacity of red clover, used its tissue fluid as such for the purpose without filtering or centrifuging.

Hydrogen-ion concentration and buffering capacities were determined electrometrically as described elsewhere (Iyengar, A. V. V., *J. Indian Inst. Sci.*, 1928, **11A,** 103). The quantity of sap used was throughout 2 c.c. It usually took 30 mins. for the hydrogen electrode to attain equilibrium.

Results.—The first experiment was to find out the effect of keeping, in the laboratory as well as in ice-room, on the initial acidity and buffering capacities of sandal tissue fluids. Results, taken at random from a large number of determinations, are recorded in Tables I and II.

TABLE I.

Effect of keeping on the initial acidity of sandal saps.

Tissue fluids from	Initial pH	pH after keeping			
		in the laboratory for			in the ice-room for 24 hrs.
		2 hrs.	4 hrs.	8 hrs.	
Healthy leaf—					
Sample I ..	5·45	5·45	5·45	5·45	5·45
Sample II ..	5·50	5·50	..	5·50	5·50
Sample III ..	5·40	..	..	5·40	5·30 (after 48 hrs.)
Spiked leaf ..	5·00	5·00	5·00	5·00	5·00
Healthy root ..	5·85	..	..	5·85	..

TABLE II.

Effect of keeping on the buffering capacities of sandal tissue fluids.

A. HEALTHY LEAF SAP (2 c.c.)			B. SPIKED ROOT SAP (2 c.c.)		
Alkali c.c.	pH		Acid c.c.	pH	
	immediately after pressing	4 hrs. after pressing		immediately after pressing	4 hrs. after pressing
0·0	5·50	5·50	0·0	5·15	5·15
0·5	5·70	5·65	0·2	4·85	4·85
1·5	6·30	6·30	0·5	4·60	4·60
2·5	6·85	6·80	1·0	4·45	4·40
3·5	7·20	7·25	2·0	4·20	4·30
3·5	7·50	7·55	3·0	4·10	4·10
5·5	7·80	7.80	5·0	4·00	4·05
6·5	8·05	8·00			

It is clear from the above that the expressed juice of sandal, healthy or spiked, does not change in pH on keeping in the laboratory for about 8 hrs., or in ice-room for 24 hrs. Other workers (Haas, A. R. C., *loc. cit.*; McLenden, J. F., and Sharp, P. F., *J. Boil. Chem.*, 1919, **38**, 531), however, found that reactions of plant tissue fluids changed on keeping. The buffering capacities remained fairly unaltered for 4 hrs. in the laboratory. This also shows the close agreement between duplicate determinations.

Sulphuric acid and acetic acid as titres.—At first, sulphuric acid, acetic acid and sodium hydroxide were used as titres. The results of these titrations are given graphically in Fig. 1. The use of sulphuric acid was discontinued later, when it was found that working with root and wood saps, even small additions of this titre gave large pH shifts, rendering their measurements difficult. Subsequently, therefore, acetic acid was used instead, since large quantities of this titre would have to be added to the saps to bring about significant shifts in their pH, while the errors due to the resulting dilution would also be negligible (Clark, *Determination of Hydrogen Ions*, 1928).

Further, as organic acids are among the metabolic products of the spike-disease of sandal, one way of simulating the condition of disease in the healthy plant is by addition of known quantities of one

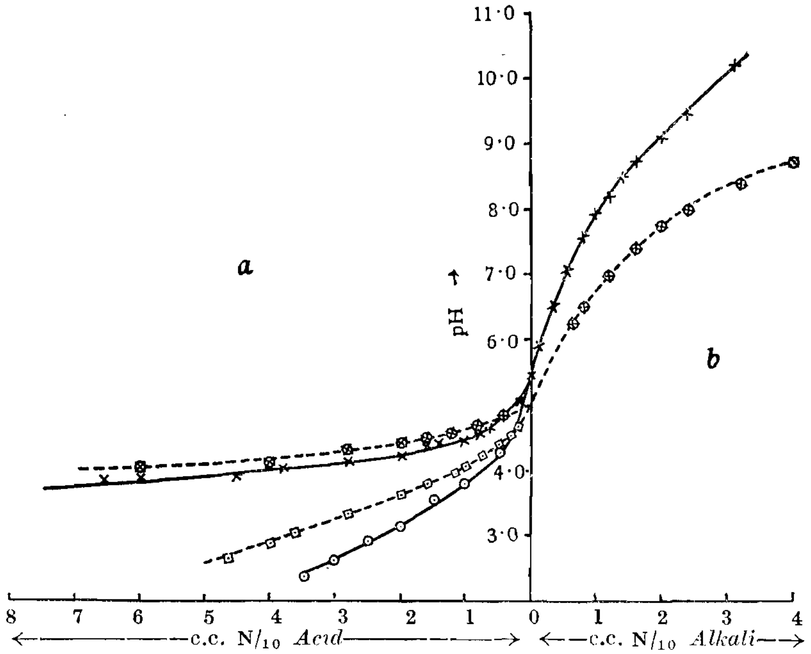

Fig. 1.

Titration curves of healthy and spiked leaf tissue fluids.

a ⊠---⊠ Spiked, ×——× Healthy } with CH_3COOH.

□---□ Spiked, ○——○ Healthy } with H_2SO_4.

b ⊠---⊠ Spiked, ×——× Healthy } with NaOH.

of the metabolic organic acids to healthy tissue fluid till its pH shifts to that of the spiked. Such acid requirements or buffering capacities of healthy tissue fluids would reasonably be a measure of resistance offered by that plant towards disease, greater buffering capacity (greater acid titre) necessarily implying greater resistance. Hence, in measurements of buffering capacity in relation to disease resistance in plants (where with the onset of disease the tissues usually get more acidic), only organic acids should be chosen as titres, and titrations continued till the pH of healthy tissue fluid has shifted just beyond that of the diseased. So, in our studies mostly acetic acid was used as the titre.

The results of the electrometric titrations of the leaf, bark, wood and root tissue fluids of sandal with the different host combinations are given graphically in Figs. 2, 3, 4 and 5. These include for comparison also sandal grown without a host plant and spiked sandal. In all these cases, titrations (only against acetic acid) were made till the initial pH shifted beyond that of the spiked (*i.e.*, by about 0·5 of a unit). From these graphs are calculated the quantities of titre required to shift the pH by 0·5 of a unit from the initial value (Table III). These values are taken as a measure of the buffering capacities of the various tissue fluids.

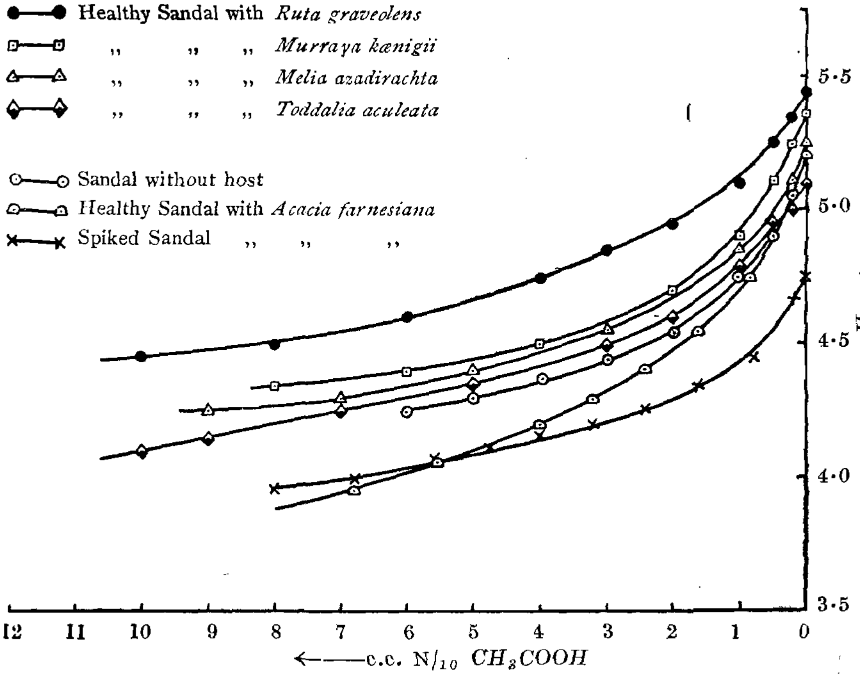

Fig. 2.

Titration curves of tissue fluids of Sandal-Leaf.

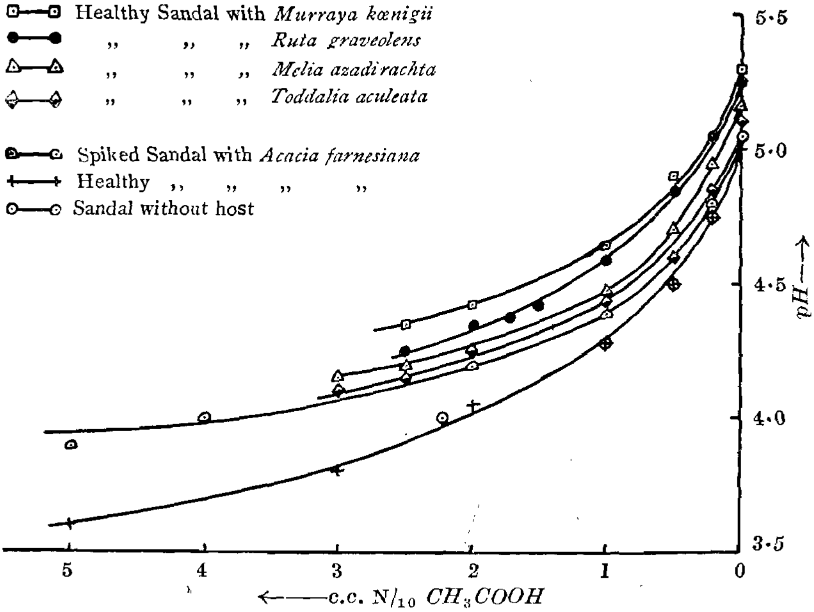

Fig. 3.

Titration curves of tissue fluids of Sandal-Bark.

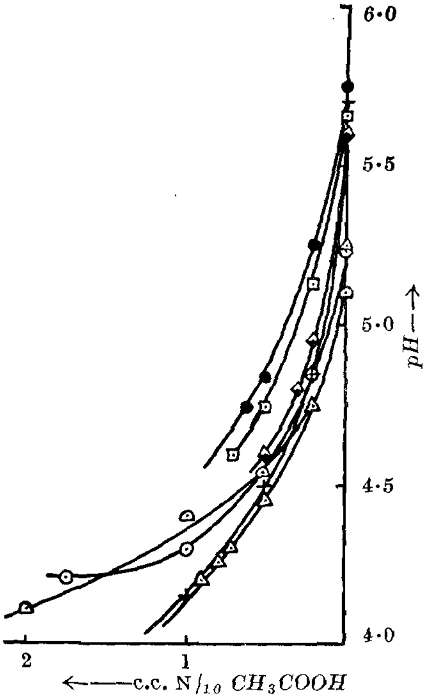

Fig. 4.

Titration curves of tissue fluids of Sandal-Wood. Legends as in Fig. 3.

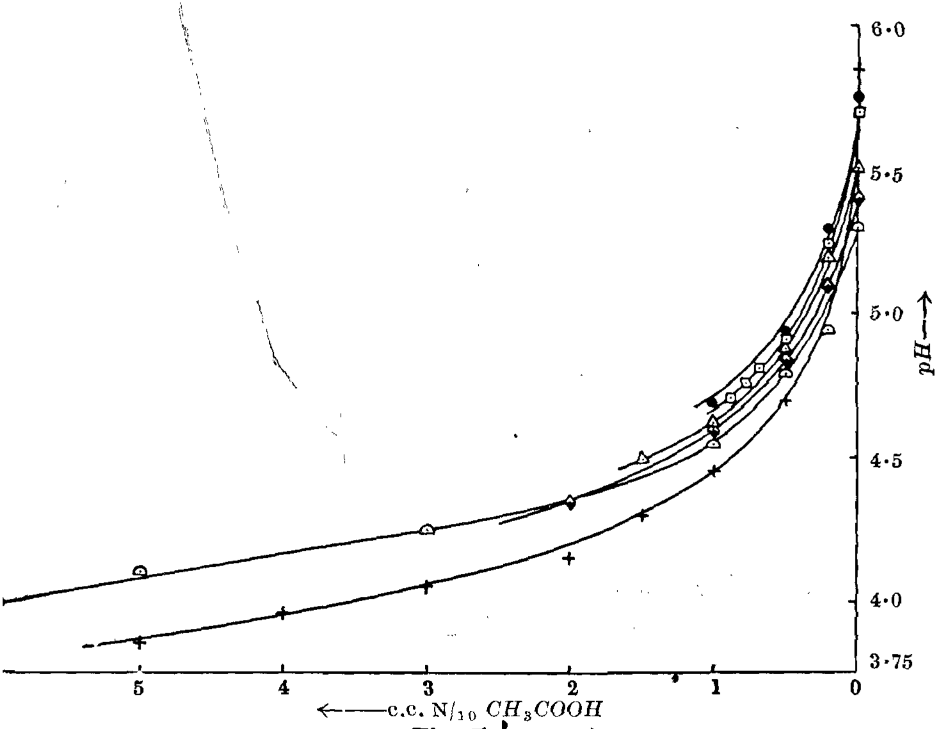

Fig. 5.

Titration curves of tissue fluids of Sandal-Root. Legends as in Fig. 3.

TABLE III.

Buffering capacities of tissue fluids of sandal grown with different host plants.

Sandal grown in combination with	c.c. of 0·1 N acetic acid needed for a shift in pH by 0·5 of a unit from the initial value of the tissue fluids of			
	Leaf	Bark	Wood	Root
Ruta graveolens ..	1·70 (5·50)	0·65 (5·25)	0·20 (5·75)	0·20 (5·75)
Murraya kœnigii ..	1·25 (5·35)	0·60 (5·30)	0·20 (5·65)	0·20 (5·70)
Melia azadirachta ..	1·50 (5·25)	0·55 (5·15)	0·20 (5·25)	0·40 (5·50)
Toddalia aculeata ..	2·00 (5·10)	0·60 (5·10)	0·15 (5·60)	0·40 (5·40)
Acacia farnesiana ..	0·45 (5·40)	0·55 (5·00)	0·05 (5·70)	0·08 (5·85)
Without host ..	1·00 (5·25)	0·45 (5·05)	0·30 (5·25)	....

The figures in brackets in the above table refer to the initial pH of th various tissue fluids.

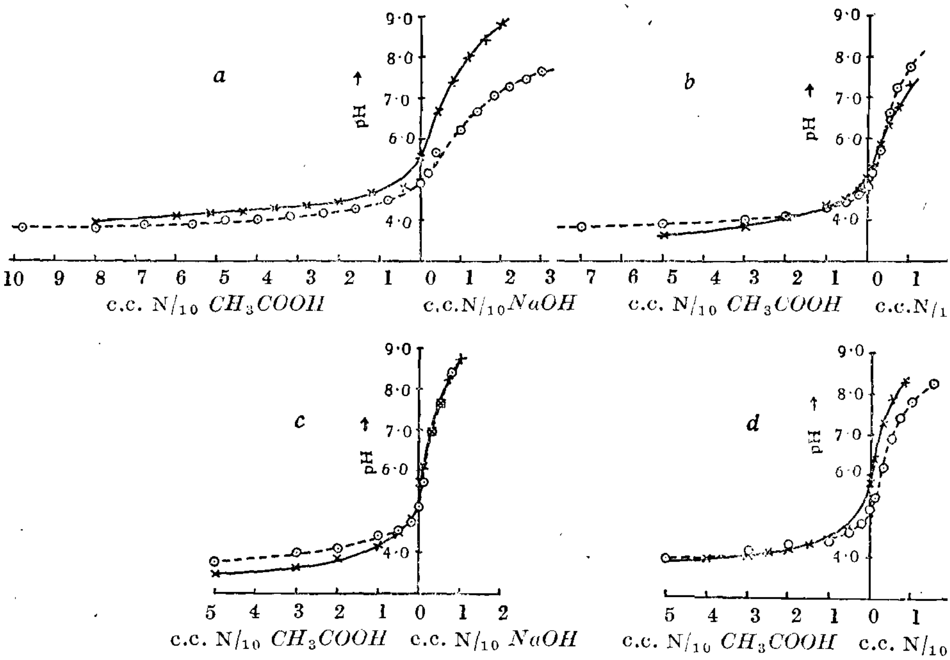

Fig. 6.

Titration curves of healthy and spiked Sandal tissue fluids.

a Leaf.	*c* Wood.	×—× Healthy
b Bark.	*d* Root.	o---o Spiked

Fig. 6 gives the general form of curves obtained with leaf, wood, bark and root of healthy and spiked sandal tissue fluids as titrated against acetic acid and sodium hydroxide. These titrations were performed with tissue fluids from six healthy and four spiked sandal plants. The corresponding titration curves were constructed and from these the buffer index = calculated according to van Slyke (*J. Biol. Chem.*, 1922, **52**, 525). These values are compiled in the following table.—

TABLE IV.

Buffer index of healthy and spiked sandal tissue fluids.

Tissue fluid from	Condition of sandal	Sample	BUFFER INDEX					
			pH					
			Initial	5—4	5·5—4·5	5·5—6·5	6—7	6·5—7·5
Leaf	Healthy ..	1	5·45	..	..	..	..	..
	(From Fig. 1 with sulphuric acid)	..	..	(0·014)	..	..	..	..
		..	..	0·250	..	0·0144	0·0144	0·0137
		2	5·50	0·343	0·094	0·0137	0·0175	0·0198
		3	5·45	0·410	..	0·0274	0·0327	0·0388
		4	5·50	0·435	0·174	0·0281	0·0319	0·0314
		5	5·30	0·383	..	0·0350	0·0395	0·0440
		6	5·30	0·393	..	0·0198	0·0228	0·0258
		7	5·35	0·410	..	0·0213	0·0228	0·0274
	Average ..		5·40	0·368	0·134	0·0228	0·0259	0·0287
	Spiked ..	1	5·00	..	..	..	..	..
	(From Fig. 1 with sulphuric acid)	..	..	(0·052)	..	0·0230	0·0290	0·0350
		2	5·00	..	..	0·0426	0·0547	0·0722
		3	4·95	..	..	0·0289	0·0380	0·0570
	Average ..		5·00	..	..	0·0315	0·0406	0·0547
Bark	Healthy ..	1	5·00	0·1525	..	0·0133	0·0114	0·0171
		2	5·00	0·1150	..	0·0133	0·0152	0·0247
		3	5·00	0·1525	..	0·0132	0·0152	..
	Average ..		5·00	0·1400	..	0·0139	0·0139	0·0209

TABLE III.

Buffering capacities of tissue fluids of sandal grown with different host plants.

Sandal grown in combination with	c.c. of 0·1 N acetic acid needed for a shift in pH by 0·5 of a unit from the initial value of the tissue fluids of			
	Leaf	Bark	Wood	Root
uta graveolens ..	1·70 (5·50)	0·65 (5·25)	0·20 (5·75)	0·20 (5·75)
urraya kœnigii ..	1·25 (5·35)	0·60 (5·30)	0·20 (5·65)	0·20 (5·70)
elia azadirachta ..	1·50 (5·25)	0·55 (5·15)	0·20 (5·25)	0·40 (5·50)
oddalia aculeata ..	2·00 (5·10)	0·60 (5·10)	0·15 (5·60)	0·40 (5·40)
cacia farnesiana ..	0·45 (5·40)	0·55 (5·00)	0·05 (5·70)	0·08 (5·85)
ithout host ..	1·00 (5·25)	0·45 (5·05)	0·30 (5·25)	....

The figures in brackets in the above table refer to the initial pH of the arious tissue fluids.

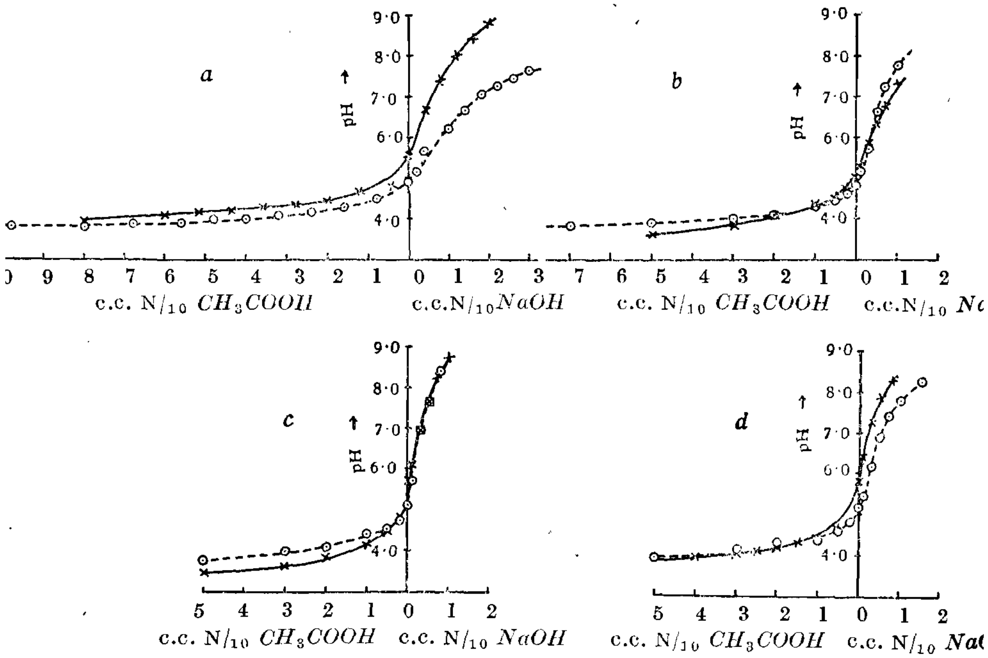

Fig. 6.

Titration curves of healthy and spiked Sandal tissue fluids.

a	Leaf.	*c*	Wood.	×—×	Healthy
b	Bark.	*d*	Root.	○--○	Spiked

Fig. 6 gives the general form of curves obtained with leaf, wood, bark and root of healthy and spiked sandal tissue fluids as titrated against acetic acid and sodium hydroxide. These titrations were performed with tissue fluids from six healthy and four spiked sandal plants. The corresponding titration curves were constructed and from these the buffer index = calculated according to van Slyke (*J. Biol. Chem.* 1922, **52**, 525). These values are compiled in the following table.—

TABLE IV.

Buffer index of healthy and spiked sandal tissue fluids.

Tissue fluid from	Condition of sandal	Sample	BUFFER INDEX					
			pH					
			Initial	5—4	5·5—4·5	5·5—6·5	6—7	6·5—7·5
Leaf	Healthy ..	1	5·45	..	..	..	..	..
	(From Fig. 1 with sulphuric acid)	..	..	(0·014)	..	..	..	..
		..	..	0·250	..	0·0144	0·0144	0·0137
		2	5·50	0·343	0·094	0·0137	0·0175	0·0198
		3	5·45	0·410	..	0·0274	0·0327	0·0388
		4	5·50	0·435	0·174	0·0281	0·0319	0·0314
		5	5·30	0·383	..	0·0350	0·0395	0·0440
		6	5·30	0·393	..	0·0198	0·0228	0·0258
		7	5·35	0·410	..	0·0213	0·0228	0·0274
	Average ..		5·40	0·368	0·134	0·0228	0·0259	0·0287
	Spiked ..	1	5·00	..	..	..	..	..
	(From Fig. 1 with sulphuric acid)	..	..	(0·052)	..	0·0230	0·0290	0·0350
		2	5·00	..	..	0·0426	0·0547	0·0722
		3	4·95	..	..	0·0289	0·0380	0·0570
	Average ..		5·00	..	..	0·0315	0·0406	0·0547
Bark	Healthy ..	1	5·00	0·1525	..	0·0133	0·0114	0·0171
		2	5·00	0·1150	..	0·0133	0·0152	0·0247
		3	5·00	0·1525	..	0·0132	0·0152	..
	Average ..		5·00	0·1400	..	0·0139	0·0139	0·0209

TABLE IV.—(*Contd.*)

Tissue fluid from	Condition of sandal	Sample	BUFFER INDEX					
				pH				
			Initial	5—4	5·5—4·5	5·5—6·5	6—7	6·5—7·5
Bark	Spiked ..	1	4·85	0·1525	..	0·0114	0·0114	0·0133
		2	5·00	0·1900	..	0·0114	0·0133	0·0152
	Average ..		4·90	0·1713	..	0·0114	0·0124	0·0143
Wood	Healthy ..	1	5·80	0·0800	0·0250	..	0·0095	0·0076
		2	5·70	0·0675	0·0200	..	0·0095	0·0076
		3	5·45	0·0950	..	0·0133	0·0114	0·0095
	Average ..		5·65	0·0808	0·0225	0·0133	0·0101	0·0082
	Spiked ..	1	5·10	0·1425	..	0·0076	0·0076	0·0076
		2	5·35	0·1700	..	0·0076	0·0076	0·0114
	Average ..		5·20	0·1562	..	0·0076	0·0076	0·0095
Root	Healthy ..	1	5·85	0·1500	0·0450	..	0·0095	0·0114
		2	5·85	0·2750	0·0725	..	0·0114	0·0114
		3	6·30	0·1850	0·0450	..	..	0·0114
		4	5·90	0·2180	0·0650	..	0·0114	0·0152
		5	6·05	0·1850	0·0450	..	0·0114	0·0152
	Average ..		6·00	0·2026	0·0545	..	0·0109	0·0129
	Spiked ..	1	5.15	0·0180	..	0·0076	0·0133	0·0152
		2	5·45	0·3300	0·0750	0·0095	0·0114	0·0114
		3	5·30	0·3430	..	0·0095	0·0152	0·0190
	Average ..		5.30	0·2303	0·0750	0·0089	0·0133	0·0152

DISCUSSION.

From Tables III and IV, it is clear that, in all the cases studied, initial acidity is highest with leaf and lowest with the root, bark and wood having corresponding intermediate values. Such gradient reactions have been recorded previously in other plant tissue fluids as well (Haas, A. R. C., *loc. cit.*; Gustafson, F. G., *Amer. J. Bot.*, 1924, **11**, 1). The acidity, however, of the sap from any tissue of the spiked plant is higher than that of the corresponding tissue from healthy sandal. This is in keeping with the general finding that the acidity of the tissue fluids of diseased plants is higher than that of the corresponding healthy ones (Hurd, A. M., *loc. cit*; Wagner, R. J., *Zentr. Bakt. Parasitenk.*, *Abt. II.*, 1916. **44**, 708; Laurent, M. E., *loc. cit.*; Robertson, I. M., and Smith, A. M., *Biochem. J.*, 1931, **25**, 768).

Leaf, again, has the highest buffering capacity, irrespective of host combinations or the physiological condition of the sandal plant. Comparing spiked and healthy tissue fluids, spiked leaf tissue fluid is more buffered than healthy both against acid (acetic or sulphuric) and alkali (graphs 1 and 6; Table IV). Especially against acetic acid is this buffering so high that additions of this titre to spiked leaf sap (2 c.c.) even in quantities far in excess of those added to the other experimental tissue fluids did not shift its pH beyond 0·5 of a unit from the initial value. This explains the absence of the values for the buffer index of spiked leaf sap against acetic acid in Table IV. The high buffering of spiked leaf tissue fluid against acid is contrary to the findings of Iyengar (*J. Indian Inst. Sci.*, 1933, **16A**, 91) *viz.*, that it is less buffered than healthy in the acid region. This discrepancy might be attributed to uncontrolled sylvicultural conditions under which the healthy and spiked plants grew and to the undefined stage of the disease.

Referring to Table III, leaf, bark, wood and root tissue fluids of sandal grown in combination with *Ruta graveolens*, *Murraya kœnigii*, *Melia azadirachta* and *Toddalia aculeata* as hosts are more buffered than those in combination with *Acacia farnesiana*. As the previous four hosts are known to impart relative immunity to sandal, while the last one renders it susceptible, it may be concluded that sandal, nourished by host plants imparting disease resistance, is more buffered than the one fed on a host rendering it susceptible, indicating that buffering capacity is a factor in controlling disease. In support of this view appears also the low buffering capacity (Table III) of the tissue fluids of leaf and bark of sandal grown without a host, which is known to easily succumb to the disease. Further, Sreenivasa Rau (*J. Indian Inst. Sci.*, 1933, **16A**, 167) observed that of the sandal plants nourished by *Pongamia glabra* and *Acacia farnesiana*, the one more buffered (*Acacia farnesiana*) is less susceptible to spike disease than the one less buffered (*Pongamia glabra*).

While there appears to be thus a significant correlation between disease resistance and buffering capacities of the tissue fluids of sandal grown with the different host plants, the possibility of other factors like the associated glucosides and alkaloids controlling resistance in sandal should not be ignored.

SUMMARY.

1. Hydrogen-ion concentration and buffering capacities of the tissue fluids of sandal, both healthy and spiked, have been studied. Healthy sandal included sandal grown with different host combinations.

2. The initial acidity and buffering capacities of the spiked tissue fluids are higher than those of healthy.

3. The following is the gradient in reaction in decreasing order, irrespective of host combinations or physiological condition of sandal plant—leaf, bark, wood and root.

4. Tissue fluids of sandal grown in combination with *Ruta graveolens*, *Murraya kœnigii*, *Melia azadirachta* and *Toddalia aculeata*—hosts imparting relative immunity to sandal—are more buffered than tissue fluids from sandal nourished on *Acacia farnesiana*, or sandal without a host, both of which are known to render sandal particularly susceptible to disease.

The possible relationships, arising out of these observations, between buffering capacity and disease resistance are discussed.

Our thanks are due to Dr. V. Subrahmanyan for the interest he has taken in this investigation.

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ESTIMATION OF TANNIN IN PLANT MATERIALS.

PART I.—*Cassia auriculata.*

By N. Srinivasan.

A number of methods have been proposed for the estimation of tannin in plant materials and these differ in principle according to the object in view. The official method (Chemists' Year Book, 1933, 953) is a 'model of empirical accuracy' and is useful for commercial purposes particularly for the evaluation of different vegetable tannin materials. It is nevertheless, somewhat tedious and requires large samples for work. The method described in the present paper is an improvement on the official one in that it requires only small samples. The estimation is also carried out more rapidly. It is based on the precipitation of tannin from the extract (Nierenstein, *Chem. Ztg.*, 1911, **35**, 31; Spiers, *J. Agric. Sci.*, 1914, **6**, 77; Hartong, *Woch. Brau.*, 1929, **46**, 11) and obtaining the tannin equivalent from the difference in the concentration of the solution before and after detannisation as determined by the Pulfrich refractometer.

EXPERIMENTAL.

Extraction of Tannin.—It was observed that finely ground powder gave turbid extracts while incomplete leaching was the result of extracting coarse material. After a number of trials, it was found that particles passing a sieve of 25-30 meshes to the inch are the most suitable for the extraction. Boiling water was found to extract best. Repeated leaching with fresh quantities of boiling water was more effective than a single extraction with a large amount of water. Four extractions thus carried out in succession was found to remove the whole of the tannin as shown by the gelatin test. The time taken for a complete extraction was about one hour.

The extract was next filtered through paper pulp. The pressed pulp was soaked in water, well beaten with a large quantity of water and poured into a funnel with its opening closed by a small piece of muslin. After filtering the tannin extract the pulp was washed repeatedly with small quantities of boiling water to remove the tannin and other soluble materials.

The following would illustrate the procedure. The water (200 c.c.) was raised to boiling in a 500 c.c. conical flask and kept simmering. The powdered plant material was divided approximately into six equal portions each one of which was dropped into the water at intervals of 5 mins. After addition of the last portion, the boiling was continued for 5 mins. and then stopped. The hot extract was then decanted into the filter. To the residue 100 c.c. of boiling water were added and the mixture kept simmering for 15 mins. and the extract again decanted out. This operation was then repeated twice with the residue, the time of boiling being 10 and 5 mins. respectively. The filtered solution and the washings were collected in a 500 c.c. measuring flask and made up to the mark. Aliquots (50 c.c.) in duplicates were evaporated on a water-bath (1½ hrs.) dried in the oven (102-104°C.) for three hours, cooled and weighed. From the weight thus obtained the total soluble matter in the bark was calculated in the usual way.

To determine the efficacy of the method, the total solid contents of extracts from three different samples of bark of *Cassia auriculata* (Tamil, *Avaram*; Canarese, *Thangadi*; Hindustani and Bengali, *Tarwar*; Cutch, *Avla*) were determined. The results have been presented in Table I.

TABLE I.

Weight of bark in grams (10% moisture basis)	Percentage of total solids as estimated		
	Specimen I	Specimen II	Specimen III
7	32·8	34·7	30·6
8	..	34·7	..
9	..	30·5	30·5
10	32·5	34·5	30·5
11	32·5	..	..
12	32·4	34·3	30·3
13	32·4	31·2	30·2

There was a slight fall in the efficiency of extraction as the quantity of bark powder was increased. For most practical purposes, however, the difference (about 0·5 per cent.) may be regarded as being negligible.

Detannisation.—Aliquots (100 c.c.) of the bark extract were shaken with 6 g. each of fat-free casein in narrow-mouthed stoppered bottles in a shaker (reciprocating type) for 15 mins. A further quantity (3 g.) of casein was then added and the shaking repeated for 10 mins. The suspension was immediately passed through filter paper (S. & S. 589). Aliquots (50 c.c.) of the filtrate were next evaporated on the water-bath, dried and weighed as previously described. From the figures thus obtained the quantities of tannin and soluble non-tannins were calculated (Table II).

TABLE II.

Weight of bark in grams (10 % moisture basis)	PERCENTAGES					
	Specimen I		Specimen II		Specimen III	
	Tans	Soluble non-tans	Tans	Soluble non-tans	Tans	Soluble non-tans
10	17·8	14·7	18·9	15·6	..	..
11	18·0	14·5	19·0	15·4	19·7	10·7
12	18·0	14·4	..	..	19·6	10·7
13	18·0	14·4	18·9	15·3	..	..

It may be seen from the above that there is fairly close agreement between the figures obtained for tannin or non-tannins in each case.

Total solids by the refractometer.—A few drops of the bark extract were introduced into the single cell of the Pulfrich refractometer. A sodium flame was used as the source of light and the angular position measured accurately at constant temperature (27°C.). The cell was then cleaned thoroughly, a few drops of distilled water introduced and the angular position determined as before.

Fig. 1 represents the relationship between the total solubles as

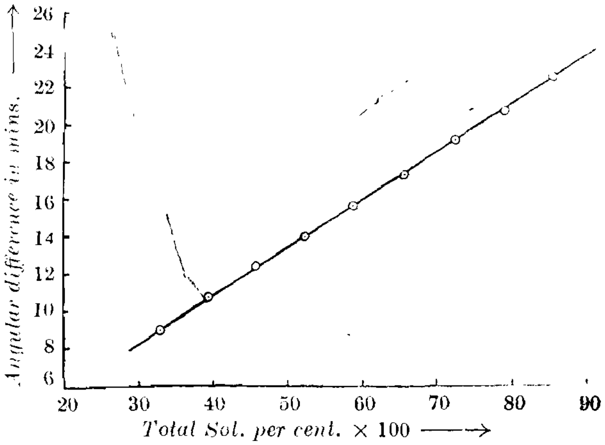

Fig. 1.

Relation between the Total Soluble Concentration of extract and difference in angular positions for the extract and distilled water.

Equation : $C = 4a - 2{\cdot}2$.

(C : Unknown concentration. a : Angular difference determined.)

determined by the evaporation method and the corresponding angular differences for distilled water and the extract.

The relationship was tested not only on extracts prepared from the same specimen but also on those from different localities. The results have been presented in Table III.

TABLE III.

	Angular difference in mins.	Concentration of the extract as read from *Fig. 1*	Concentration obtained by actual evaporation
Angle of deviation for distilled water : 66°33·2′		SPECIMEN I	
	11·9	0·45	0·46
	20·0	0·78	0·78
	18·5	0·72	0·72
	14·2	0·55	0·54
	22·0	0·86	0·84
		SPECIMEN II	
	15·2	0·59	0·56
	19·1	0·74	0·72
	12·4	0·47	0·44
	16·5	0·64	0·61
		SPECIMEN III	
	12·2	0·47	0·49
	17·5	0·68	0·69
	22·4	0·87	0·88

It may be seen from the above that there is a fair amount of agreement between values obtained from Fig. 1 and those by evaporation. The agreement is very close in the case of the particular specimen (No. I) of bark, extracts of which were used for the refractometer readings in Fig. 1. It is less marked in the case of the other two specimens, the values obtained from the refractometer readings being slightly higher or lower than those obtained by evaporation.

A straight line graph similar to Fig. 1 was obtained for the relation between the angular difference and the solid content of the solution of non-tans left after removal of tannin in the manner already described. The agreement between the figures expected from the readings and those actually found for specimen I were quite close. In the cases of specimens II and III, the difference between the figures obtained by actual evaporation and those read off from the curve were nearly of the same order as in that of total solids. These observations suggest that the slight discrepancy observed in cases of specimens II and III are due to some difference in the nature and proportion of non-tans; that the error for total solids and non-tans being of the same order, the difference representing the tannin would yield correct values irrespective of the origin of the specimen.

An attempt was made to trace the relation between the angular difference of the bark extract and the tannin content as determined by the usual evaporation method (Fig. 2). The results (Table IV) showed however that although there was some agreement in the case of the particular specimen (I) extracts of which were used for obtaining the data in Fig. 2, it was not close in the case of others (specimens II and III). This should be traced to the non-proportionality between the tannin and the non-tannins in the different extracts.

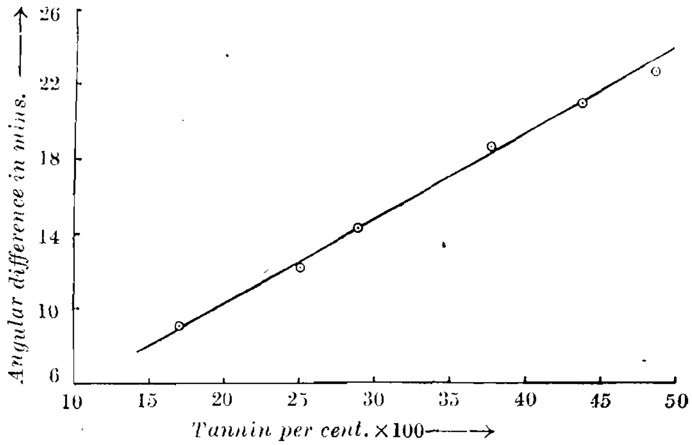

Fig. 2.

Relation between Tan strength of extract and difference in angular positions for the extract and distilled water.

Equation : $C = 2{\cdot}2a - 1{\cdot}76$.

(C : Unknown concentration. a : Angular difference determined.)

TABLE IV.

Angular difference in mins.	Percentage tannin concentration from graph	Percentage tannin concentration by evaporation
	SPECIMEN I	
11·9	0·24	0·23
20·0	0·42	0·43
18·5	0·39	0·40
14·2	0·30	0·29
22·0	0·47	0·47
	SPECIMENS II & III	
15·2	0·32	0·32
19·1	0·40	0·45
11·2	0·23	0·26
16·5	0·35	0·38

Since non-tans are primarily responsible for the discrepancy between the results calculated from the refractometric readings and those estimated by evaporation, some experiments were next carried out determining the angular deviations before and after detannisation and plotting the difference against the tannin content as obtained by the evaporation method. The results have been presented in Fig. 3.

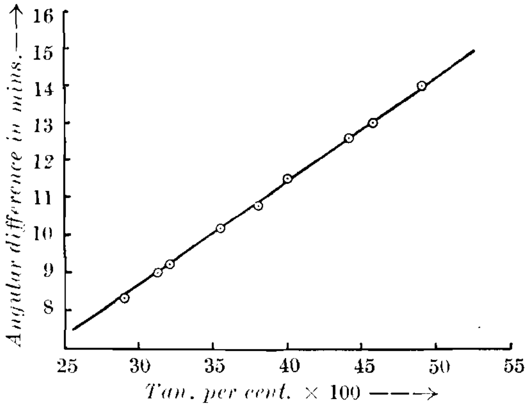

Fig. 3.

Relation between Tan strength of extract and difference in angular positions for the extract and the detannised solution.

Equation : $C = 3{\cdot}625a - 1{\cdot}375$.

(C : Unknown concentration. a : Angular difference determined.)

With a view to determining whether the relation between difference in angular deviation and tannin content holds true for all samples of bark irrespective of locality, some experiments were carried out comparing the estimates by the refractometric and the evaporation methods (Table V).

TABLE V.

Locality from which the sample was obtained	Weight of bark in grams (10% moisture basis)	Volume of extract in c.c.	Total solubles in 50 c.c. by evaporation	Non-tans in 50 c.c. by evaporation	Angular difference in mins.	Tannin per cent.	
						by evaporation	by refractometric method
Trichinopoly	10	500	0·346	0·157	10·8	18·9	18·9
Dindigul	10	500	0·335	0·157	10·3	17·8	18·0
Kopbal	10	500	0·357	0·160	11·4	19·7	20·0
Bellary	10	500	0·321	0·143	10·3	17·7	18·0
Pudukotah	9	500	0·311	0·142	9·7	18·8	18·8

It may be seen from the above that there is fairly close agreement between tannin contents as obtained by the two methods.

Estimation of tannin in small samples.— The quantity of extract required for refractometric measurements being very small, some experiments were next carried out to determine whether that method can be extended to the estimation of tannin in small quantities of bark. The trials were carried out with quantities corresponding to one-tenth of those used in the previous experiments and the results compared with those obtained in larger quantities by the evaporation method (Table VI).

The foregoing observations show that fairly accurate results can be obtained by the refractometric method though only small quantities of bark are taken. The angular positions can be read on the instrument upto one-tenth of a minute and this corresponds to an accuracy of 0·004 per cent. on the tannin concentration of the extract. The observations further suggest that in addition to its application in the analysis of commercial samples of bark or bark extract, the refractometric method can be successfully adopted in the study of biochemical problems relating to the origin and distribution of tannins in plants. The technique would render it possible to examine small samples of bark even from the living plant without appreciably affecting growth, so that it would also be of considerable assistance in the investigation of problems relating to tannin metabolism at various stages in the life of the plant.

TABLE VI.

Locality from which the sample was obtained	*Weight of bark in grams (10 % moisture basis)*	Angular difference in mins.	Percentage of tannin in bark	
			by evaporation	by refractometric method
Bellary	1·2 1·0 1·3	12·2 10·2 13·3	17·7	17·9 17·8 18·0
Dindigul	1·2 1·0	12·0 10·2	17·8	17·6 17·8
Kopbal	1·0 1·2	11·3 13·7	19·7	19·8 20·1
Pudukotah	1·2 1·0 1·1	12·9 10·7 11·8	18·8	18·9 18·7 18·8
Trichinopoly	1·2 0·9 1·0	13·0 9·9 10·9	18·9	19·1 19·2 19·1

Although the present enquiry relates primarily to the examination of the tannin in *Cassia auriculata*, the results do yet suggest that the refractometric method can be extended for the estimation of tannin in other plant materials as well. It has already been shown that the relation between the tannin contents and the difference in refractometric readings for the whole and detannised *Cassia auriculata* bark extracts can be represented by a simple equation of the type $Y=a+bX$. If similar equations can be obtained for other plant materials as well, the tannin concentrations—within a useful range—can be calculated from refractometric readings without reference to any figure specially drawn for the purpose. It is proposed therefore to extend the present enquiry to include other tannin-bearing materials as well and to work out the equation in each case. It is also hoped that it would soon be possible to construct a simple direct reading instrument that would give fairly accurate estimates of tannin contents of commercial samples of different barks and bark-extracts.

SUMMARY.

1. A simple and rapid method for the estimation of tannin in the bark of *Cassia auriculata* has been described. It is based on the measurement of the angles of deviation on the refractometer before and after

detannising the extract and calculating the tannin content from the difference.

2. For the same sample of bark, there is close correlation between the tannin contents and refractometric readings for the whole extract. The relation is not so close when extracts from different specimens are compared. This is traceable to the varying proportions of non-tans present in the different cases. To obtain accurate estimates of tannin contents, it is necessary therefore to take readings before and after detannising the extracts.

3. The application of the method to the estimation of tannin in small samples of bark and its practical significance have been discussed.

4. The extension of the method to other tannin-bearing materials as also the possibility of the construction of a simple direct reading instrument for routine estimations have been indicated.

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RAMAN EFFECT IN CERTAIN DERIVATIVES OF CYCLOHEXANE.

By G. V. Nevgi and S. K. Kulkarni Jatkar.

INTRODUCTION.

It is well known that the ortho-, meta- and para-xylenes show different Raman Spectra. H. Mlodzianovska (*Zeit. f. Physik.*, 1930, **65**, 124) investigated the influence of the position of groups in a series of disubstituted benzene derivatives on the Raman Spectra and has shown that some of the frequencies are common to all the isomerides, some to ortho and meta, meta and para or ortho and para and some are peculiar to each isomeride. Ganesan and Thatte (*Zeit. f. Physik.*, 1931, **70**, 131) have obtained identical Raman Spectra with the ortho-, meta- and para-toluidines, in contradiction with the results of H. Mlodzianovska in the three toluidines. Recently M. E. High (*Phys. Rev.*, 1931, **38**, 1837) has shown in four such series of isomers, a regular increase in the value of the lower frequencies in the order ortho, meta and para.

The purpose of the present investigation is to study the Raman Spectra of the ortho-, meta- and para-compounds in order to see whether the position of the substituted groups influences the Raman Spectrum of a molecule. For this, compounds belonging to the cyclohexane series were chosen because they were free from such troubles as the discolouration due to exposure to light or the photochemical decomposition such as occurring in the toluidines, etc.

The following table gives the physical properties of the substances investigated. The densities and refractive indices were determined at 25° and 30° calculated for 20° in order to compare with the figures given in literature (Landolt Börnstein & International Critical Tables).

Ganesan and Venkateswaran (*Ind. Jour. Phys.*, 1929, **4**, 195) and Petrikaln and Hochberg (*Phys. Chem.*, 1929, **B. 3**, 226) have examined the cyclohexane and the latter authors have examined the cyclohexanol also in an incomplete manner. During the progress of this work J. Weiler (*Z. Physik.*, 1931, **69**, 586) published his results on the Raman Spectra in cyclohexane and cyclohexene.

Since the completion of our work, the Raman Spectra of cyclohexane and some of its derivatives have been examined by Krishnamurti (*Ind. Jour. Phys.*, 1932, **6**, 543), Godchot and co-workers (*Comptes Rendus*, 1932, **194**, 176 and 1574) and Wood and Collins

TABLE I.

	$D_{20/4}$		N_{D20}		B.P. (685 mm.)
	Authors	Literature	Authors	Literature	
Cyclohexane	0·7846	0·779	1·4244	1·427	77°·5
Methylcyclohexane ..	0·7755	0·764	1·4231	1·423	97°·0
m–Dimethylcyclohexane	0·7768	0·771	1·4242	1·429	117°·5
Cyclohexene	0·8349	0·810	1·4454		81°·0
Cyclohexyl acetate ..	0·9669		1·4417		87° (35 mm.)
Cyclohexyl propionate ..	0·9539		1·4403		93° (35 mm.)
Cyclohexanol	0·9516	0·949	1·4654	1·4659	156°
o–Methylcyclohexanol ..	0·9354	0·928	1·4607	1·463	160°
m–Methylcyclohexanol ..	0·9246	0·917	1·4560	1·458	167°·5
p–Methylcyclohexanol ..	0·9202	0·917	1·4567	1·455	169°
Cyclohexanone	0·9665	0·949	1·4503	1·4526	70° (45 mm.)
o–Methylcyclohexanone	0·9325	0·930	1·4477		67° (23 mm.)
m–Methylcyclohexanone	0·9184	0·914	1·4460		70° (25 mm.)
p–Methylcyclohexanone	0·9171	0·912	1·4441		68° (23 mm.)

(*Phys. Rev.*, 1932, **42,** 386), that of cyclohexane by Wood and Collin (*loc. cit.*) and Morris (*Ibid.*, 1931, **38,** 141). The work of these author is more or less in agreement with ours.

Recently Miller and Piaux (*Compt. Rend.*, 1933, **197,** 412) hav investigated the Raman Spectra of the *cis* and *trans* space isomers c ortho-dimethyl cyclohexane prepared by fractionating the product c hydrogenation of orthoxylene. The derivatives examined by us ar probably mixtures of *cis* and *trans* compounds. All these authors hav obtained Raman lines only with the 4046 and 4358 mercury lines. I this investigation, Raman lines with the 3125, 3131, and the triple 3650, 3654 and 3662 mercury lines have been obtained for cyclohexane methylcyclohexane, methylcyclohexanol and cyclohexene by usin quartz tube.

The spectrograph used was Hilger's E 316. The letters use in the tables indicate the exciting mercury lines as given in th following table:

TABLE II.

Wave-lengths and symbols of the mercury arc lines.

Wave-length in Å	Wave-number cm.$^{-1}$	Symbol
4358·3	22938	a
4347·5	22995	b
4339·2	23039	c
4077·8	24516	d
4046·6	24705	e
3662·9	27293	f
3654·8	27353	g
3650·2	27388	h
3341·6	29917	A
3131·6	31923	B
3125·6	31985	C
3021·6	33085	D
2967·2	33692	E

The Raman frequencies of the different cyclohexane derivatives are given in the following tables with their intensity and exciting lines shown within brackets, the data obtained by other workers being also shown for comparison.

TABLE III.

Cyclohexane.

Petrikaln and Hochberg[1]	Ganesan and Venkateswaran[2]	Daure[3]	Weiler[4]	Authors
..	383(0) (ae)	..	365(0) (ae)	393(1) (ae)
..	420(0) (ae)	430(ae)	424(0) (ae)	431(1) (aef)
..	478(0) (e)	..	..	..
..	608(0) (ae)	..	..	..
801(5) (ae)	800(4) (abcde)	800(ae)	803(4) (ade)	808(6) (abcdefghBC)
895(1) (a)	..	..	896(0) (e)	..
925(1) (a)	..	..	..	..
..	..	..	971(0) (a)	..
..	992(2) (abcde)	..	..	..
1030(4) (ae)	1028(2) (ade)	1030(ae)	1029(2) (acde)	1036(5) (abegABC)
1082(5) (a)	..	..	..	..
1162(5) (a)	1157(1) (ae)	1160(ae)	1156(1) (abde)	1162(2) (deh)
1267(4) (ae)	1268(3) (ae)	1270(ae)	1263(1) (ade)	1270(5) (efghABC)
1350(4) (a)	1346(2) (ae)	1360(ae)	..	1354(2) (eAC)
1442(4) (ae)	1445(3) (ace)	1440(ae)	1444(1) (ace)	1448(5) (aefhABC)
..	..	2660(ae)	..	2675(2) (e)
..	..	2700(ae)	..	..
2867(5) (ae)	2853(4) (adefh)	2860(ae)	2850(4) (adefgh)	2856(6) (adeBCD)
..	2890(1) (de)	..	..	..
..	2921(3) (defh)	..	2920(2) (adefgh)	..
2944(4) (ae)	2935(3) (adefgh)	2931(ae)	2941(2) (adefgh)	2938(6) (adefghBD)

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[1] Petrikaln and Hochberg, *Zeit. f. Phys. Chem.* B., 1929, **3**, 217 and 405.

[2] Ganesan and Venkateswaran, *Ind. Jour. Phys.*, 1929, **4**, 196.

[3] Daure, *Annales de Phys.*, 1929, **12**, 375.

[4] Weiler, *Zeit. f. Physik.*, 1931, **69**, 586.

TABLE IV.

Cyclohexene.

Lespieau and Bourguel[5]	Weiler[6]	Authors
..	173(0) (a)	..
..	292(0) (ae)	..
396(a)	393(1) (ace)	400(3) (aB)
..	..	467(1) (a)
..	494(1) (abce)	501(1) (aefg)
..	649(0) (ae)	651(1) (aefh)
..	731(0) (e)	735(1) (aeg)
825(a)	826(4) (abcde)	832(5) (abcdeghBC)
..	879(1) (ade)	883(2) (aegh)
..	905(1) (ae)	909(2) (ae)
..	963(1) (ade)	969(2) (aehABC)
1029(a)	1036(1) (ade)	1043(0) (ef)
1072(a)	1058(1) (ade)	1072(3) (aefhABC)
..	..	1144(1) (e)
1219(a)	1220(1)	..
..	..	1231(4) (aeABC)
1276(a)	1266(2) (abcde)	1274(3) (egh)
..	..	1355(1) (ehC)
1429(a)	1430(2) (ae)	..
1462(a)	1448(1) (abce)	1447(4) (aefghABC)
1654(a)	1650(2) (ae)	1655(4) (aghABCD)
2807(a)	2835(3) (adefh)	2842(2) (ehCD)
2868(a)	2862(2) (ade)	2876(1) (CD)
..	2884(2) (aef)	2887(2) (aeD)
2916(a)	2914(2) (adeh)	2919(2) (hBCD)
2944(a)	2940(2) (aefgh)	2946(5) (adeghBCD)
3024(a)	3024(3) (adefgh)	3033(4) (aefhBCDE)

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[5] Lespieau and Bourguel, *C. R.*, 1930, **190**, 1504.

[6] Weiler, *Zeit. f. Physik.*, 1931, **69**, 586.

TABLE V. *Raman Spectra of Cyclohexane and its Derivatives.*

Cyclohexene	Cyclohexane	Methylcyclohexane	*m*-Dimethyl cyclohexane	Cyclohexanol	*o*-Methyl Cyclohexanol	*m*-Methyl cyclohexanol
400(8)	393(3)					
	431(3)	414(2)	427(4)			426(4)
467(3)		454(2)			443(2)	457(4)
501(3)						
		551(2)	549(5)	558(2)	522(6) 575(2)	551(4)
651(3)						
735(3)	808(10)	773(10)	767(7)	798(8)	768(6)	773(6)
832(10)		848(4)	847(3)	853(2)	843(2)	
883(4) 909(4)		895(4)	955(2)			
969(4)		972(4)	992(3)		986(4)	974(4)
1043(0) 1072(7)	1036(8)	1036(4)	1066(7)	1028(6)	1039(2) 1087(2)	1044(4)
1144(3)	1162(3)	1165(4)	1170(6)	1147(2)	1145(4)	1151(2)
1231(0) 1274(7)	1270(8)	1267(4)	1223(2) 1269(3)	1259(6)	1254(6)	1257(4)
1355(3)	1354(3)	1348(4)	1353(6)	1364(2)	1354(4)	1354(4)
1447(10)	1448(8)	1452(8)	1456(7)	1446(8)	1458(8)	1448(6)
1641(10)						
	2675(3)				2665(2)	
2842(4)						
2876(3)	2856(10)	2855(10)	2855(10)	2859(10)	2865(8)	2862(8)
2887(4)						
2919(4)						
2946(4)	2938(10)	2934(10)	2936(10)	2939(10)	2936(10)	2933(10)
3033(4)						

TABLE V. *Raman Spectra of Cyclohexane and its Derivatives.*—(Contd.)

p-Methyl cyclohexanol	Cyclohexyl acetate	Cyclohexyl propionate	Cyclohexanone	*o*-Methyl cyclohexanone	*m*-Methyl cyclohexanone	*p*-Methyl cyclohexanone	Vibrator
		269(2)					
	303(4)	304(2)	314(2)	312(2)			
394(2)				411(2)	400(3)	386(6)	
			423(4)				
482(4)		462(2)					
			499(2)		511(3)	500(6)	
	559(2)			577(5)			
649(2)			656(6)	663(8)	641(8)	692(4)	
779(6)	806(6)	806(6)	756(6)	725(8)	751(8)	750(8) 808(4)	Ring
			843(6)	843(5)	827(5)		
	901(2)	910(2)			883(3)		
	970(2)		955(2)	988(5)	961(5)		
1051(4)	1033(6)	1032(4)	1030(6)	1053(3)	1051(3) 1086(3)	1013(6) 1088(4)	
1151(2)	1164(2)	1160(2)	1131(4)	1133(3)	1120(5)	1125(4) 1191(2)	
1228(4) 1252(2)	1264(4)	1264(4)	1230(2) 1266(2)	1254(2)	1219(5) 1271(3)	1248(2)	
1359(4)	1348(2)	1369(2)	1322(4) 1362(2)	1317(5)	1333(5)	1321(2)	
1457(6)	1450(6)	1449(6)	1451(8)	1451(8)	1425(3) 1458(8)	1463(6)	CH_2
			1714(8)	1712(8)	1708(8)	1715(6)	C=O ketone
	1742(2)	1738(2)					C=O ester
2862(8)	2865(8)	2863(8)	2860(10)	2859(10)	2872(8)	2879(0)	$C_6H_{11} \rightarrow H$
2944(5)	2939(10)	2943(10)	2957(10)	2943(8)	2947(10)	2955(8)	$C \rightarrow H$
							$\geqslant C \rightarrow H$

DISCUSSION.

The results are summarised in Table V. In the following discussion attempt has been made to identify the prominent Raman lines with the vibrations of the linkages taking into consideration data obtained under the same conditions of dispersion and resolution. The more detailed discussion can be made only after preparing these compounds in a pure condition and using a spectrograph with a higher dispersion.

According to Sacshe–Mohr multiplaner strainless ring structure cyclohexane can exist as a *chair* and a *cradle* form which will create two differently situated C–H linkages. This fact taken along with the *cis-trans* isomerism in the disubstituted derivatives shows the complexity of the problem and is probably the cause of disagreeing physical data of these substances. Because of the possibility of isomerism the study of Raman Spectra of cyclohexane compounds is considerably more interesting than the corresponding study of benzene derivatives. The strong frequency 3060 in benzene due to aromatic C–H linkage is absent in all the compounds and two prominent frequencies 2850 and 2950 due to aliphatic C–H are present. These two frequencies may be due to the vibration of $C \rightarrow H$ and $C_6H_5 \rightarrow H$ with the same value for the binding energy. In cyclohexene the frequency 2850 is split up into three components 2835, 2868 and 2882 and the second frequency 2930 is split up into two components 2919 and 2946, the increased number of frequencies being due to the presence of C=C in the ring creating two differently placed C–H linkages. Besides aliphatic C–H frequencies present in cyclohexene, a strong line also appears at 3033 which may be identified as due to the $H–C\leqslant$ linkage. This frequency is not due to the aromatic C–H because it is also present in amylene.

The frequency 1450 originating from the transverse vibration of C–H in CH_2 is strongly present in all the compounds. In cyclohexene a strong frequency appears at 1655 originating from the C=C linkage. The two esters cyclohexyl acetate and propionate show a frequency at 1735 which is due to C=O group in esters. The cyclohexanone and ortho-, meta- and para- methyl cyclohexanones show a strong frequency at 1705 which is due to the presence of the C=O group in a ketone. The C=O frequency in esters has a higher value than the C=O frequency in ketones (*cf.* Dadieu and Kohlrausch, *Ber.*, 1930, **63**, 251).

The shifts 1100–1450 which are usually regarded as due to transverse oscillation of hydrogen show the characteristics of *cis* and *trans* isomers in the ortho-dimethyl cyclohexane investigated by Miller and Piaux (*loc. cit.*), 1164 cm.$^{-1}$ and 1355 cm.$^{-1}$ being characteristic of *trans* and 1260 cm.$^{-1}$ and 1053 cm.$^{-1}$ of *cis*. It is interesting to note that in cyclohexane 1164 and 1355 have the same intensity while 1260 goes with 1036 cm.$^{-1}$ although the latter is regarded as due to C–C vibration.

It appears that the compounds isolated by Miller and Piaux are more likely to be the '*cradle*' and '*chair*' forms of the cyclohexane derivative rather than being space isomers.

The large number of frequencies in cyclohexene in the range 1100–1400 is due to the transverse vibrations of α and β C–H with respect to C=C present in this compound. The occurrence of similar frequencies in terpenes is due to the same cause and will be discussed in a later paper.

A strong frequency at about 800 is characteristic of the oscillation of a closed ring. Its values in different compounds are:

(1) Cyclohexane	808
(2) Methylcyclohexane	773
(3) *M*-Dimethyl cyclohexane ..	767
(4) Cyclohexene	832
(5) Cyclohexyl acetate	806
(6) Cyclohexyl propionate	806

In all the compounds there is a large number of frequencies, between approximately 200 and 1300 which are apparently due to the vibrations of carbon chains C–C, C–C–C, C–C–C–C and so on. This region is especially rich in lines in cyclohexene which may be due to the additional vibrations of the C=C against the rest of the carbon chains. The frequencies from 600–1300 may be due to the oscillations between the C–C bonds and those from 200–600, due to the C–C–C bonds.

Comparison of the ortha-, meta- and para-compounds.

Methylcyclohexanols.

In methylcyclohexanols the frequencies higher than 1000 are all common to the three isomers. Moreover, the values of these frequencies for cyclohexanol also are the same as given below:

TABLE VI.

Cyclohexanol	Ortho-methyl-cyclohexanol	Meta-methyl-cyclohexanol	Para-methyl-cyclohexanol	Vibrator
1028	1039	1044	1051	C—C
1147	1145	1151	1151	
1259	1254	1257	1252	
1364	1354	1354	1359	$—CH_2—$
1446	1458	1448	1457	
2859	2865	2862	2862	C—H
2939	2936	2933	2944	

This shows that the higher frequencies in this series do not change in value to a measurable extent even if we pass from the cyclohexanol *to the next member, methylcyclohexanol. The position of the substituted* groups also does not influence the values of these frequencies.

The frequencies of the OH *group.*

In the cyclohexanol and methyl cyclohexanols, the OH group vibrates against the rest of the molecule giving rise to a particular frequency. The following are the values for these frequencies in different compounds, and A_0 the heat of dissociation of the R–OH linkage calculated from these frequencies.

		Observed frequency	Calculated A_0
(1)	Cyclohexanol	*798*	105·5
(2)	Ortho-methylcyclohexanol	*768*	100·5
(3)	Meta-methylcyclohexanol	*773*	101·7
(4)	Para-methylcyclohexanol	*779*	103·5

The heat of dissociation is of the same order as for aliphatic alcohols and the values are in harmony with the fact that orthosubstituted cyclohexanols are much more rapidly dehydrated than the corresponding para compounds (Vavon and Barbier, *Bull. Soc. Chim.*, 1931, (4) **49**, 567).

The position of the substituted groups exerts an influence on the value of frequencies lower than 700, showing a regular increase in the values as we go from ortho to meta and meta to para as can be seen below:

(1)	Ortho-methylcyclohexanol	443	522
(2)	Meta-methylcyclohexanol	457	551
(3)	Para-methylcyclohexanol cyclohexanone	482	649
(4)	Ortho-methylcyclohexanone	312	577
(5)	Meta ,, ,,	400	641
(6)	Para ,, ,,	500	692

Methylcyclohexanones.

In the methylcyclohexanones the frequencies can be classified into three groups:

(i) Frequencies appearing in all three isomers.

(ii) Frequencies appearing in any two either ortho and meta or meta and para or ortho and para compounds.

(iii) Frequencies appearing only in one isomer.

All these frequencies in the three methylcyclohexanones along with the cyclohexanone are classified in the following table:

TABLE VII.

Classification of Frequencies of the Cyclohexanones.

Cyclohexanone	Ortho-methyl-cyclohexanone	Meta-methyl-cyclohexanone	Para-methyl-cyclohexanone	Vibrator
314	312			
423	411	400	386	C–C–C
499	577	511	500	
656	663	641		
756	725		692	
		751	750	
			808	
		827		
843	843			
		883		
955		961		C–C
	988			
1030			1013	
	1053	1051		
1081		1086	1088	
1131	1133	1120	1125	
1230		1219	1191	
	1254		1248	
1266		1271		
1322	1317	1333	1321	
1362				
		1425		$-CH_2-$
1451	1451	1458	1463	
1714	1712	1708	1715	C=O
2869	2859	2872	2879	C–H
2957	2943	2947	2955	

Recently L. Piaux (*Compt. Rend.*, 1933, **197,** 1647) has reported on the Raman Spectra of *o*, *m* and *p* methylcyclohexanones. He attributes the absence of lines between 1600–1700 cm.$^{-1}$ to the small proportion of enolic forms in the ketones.

In a general way the Raman lines are in harmony with the fact that the chemical characteristics of cyclohexanones are closely parallel to aliphatic ketones.

Comparison with the Infra-red data.

In the following table, the frequencies of the Raman lines corresponding to those known infra-red spectra (J. Lecomte, *Compt. Rend.*, 1926, **183**, 27) are given for comparison:

TABLE VIII.

Raman. Infra-red.

Cyclohexane		Methyl Cyclohexane		*m*-Dimethyl cyclohexane		Cyclohexanol	
3·40	3·26	3·41	3·16	3·41	3·16	3·40	3·15
3·50	3·60	3·50	3·58	3·50	3·62	3·5	3·5
3·74	3·90						
6·91	6·97	6·89	6·97	6·87	6·97	6·92	7·00
7·39	7·56	7·43	7·40	7·39	7·40	7·34	7·48
7·87	8·2						
9·69	9·6						

Cyclohexanone		Cyclohexene		Cyclohexyl acetate	
3·38	3·03	3·30	3·26	3·40	3·03
3·49	3·60	3·52	3·58	3·49	3·6
5·84	5·93	6·04	6·22	5·74	5·90
6·89	6·97	6·92	7·00	6·90	6·87
7·35	7·10	7·39	7·35	7·43	7·43
7·57	7·57	7·86	7·68	7·92	7·98
7·91	7·77				

Lecomte found in these compounds two strong zones of absorption at 3·5μ and 7μ separated by a region of feeble absorption, composed of feeble intensity bands. "In passing from benzene compounds to cyclohexane derivatives the two principal bands 3·3μ and 6·8μ (in benzene) become longer 3·6 and 6·97μ (in cyclohexane) and 7·00μ (in cyclohexene). Introduction of methyl group makes the band 7·40μ appear very strongly. The groups CO, OH and CO in cyclohexanone, cyclohexanol and its acetate render the spectrum very simple, the feeble bands at 3·5μ and 6·5μ being entirely suppressed."

SUMMARY.

In all the derivatives of cyclohexane, the C–H bond appears in the same position as in aliphatic compounds. In general the frequencies in the region 600–1300 are identified with the C–C bonds and those from 200–600 with the C–C–C bonds.

In the methylcyclohexanols, frequencies higher than 1000 are common to all three isomers, but the smaller shifts show a regular increase in their values in the order ortho, meta and para.

The methylcyclohexanones, in addition to the individual characteristic frequencies, show as in the methylcyclohexanols a regular gradation in the smaller shifts 200–700 and are further distinguished by some frequencies which are common to ortho and meta, meta and para, and ortho and para.

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RAMAN EFFECT IN SOME TERPENES.

By G. V. Nevgi and S. K. Kulkarni Jatkar.

INTRODUCTION.

Bhagavantam and Venkateswaran (*Nature*, 1930, **125,** 237) have found, in the optical isomers of pinene, appreciable differences in the relative intensities of some of the lines, especially the line corresponding to the infra-red wavelength of about 74 *u* was particularly strong in the dextro while it was comparatively much weaker in the lævo form. The spectra of the dextro and lævo pinenes produced with ordinary and polarised light have been shown to be identical by A. Kastler (*C. R.*, 1930, **191,** 565), the differences found by Bhagavantam and Venkateswaran being attributed to impurities. The latter authors have recently published another paper (*Indian Journal of Physics*, 1932, **7,** 585) in which they obtained identical values for *l* and *d* pinene.

The purpose of the present investigation is to study a number of optical isomers having the empirical formulæ $C_{10}H_{16}$ for their Raman Spectra, in order to settle the point of their identity.

As the last three substances were available only in very small quantities, a special tube, with fused flat ends, was designed and satisfactory results were obtained with 7-8 c.c. of the liquids. The physical constants of these substances and other optical properties are discussed in a paper by one of us (S. K. K. Jatkar) and Padmanabhan in a paper under publication in the *Journal of American Chemical Society.*

RESULTS.

In the following tables, the results of the complete analysis of the Raman Spectra of all the eight isomers are given. In the case of dextro Δ^3 –carene, the results agree with those obtained by Dupont, Daure and Allard (*Bull. Soc. Chim.*, 1931, **49-50,** 1401) using the 4358 Å of mercury as exciting line.

The Raman frequencies, with their intensities, are also graphically represented in Fig. 1.

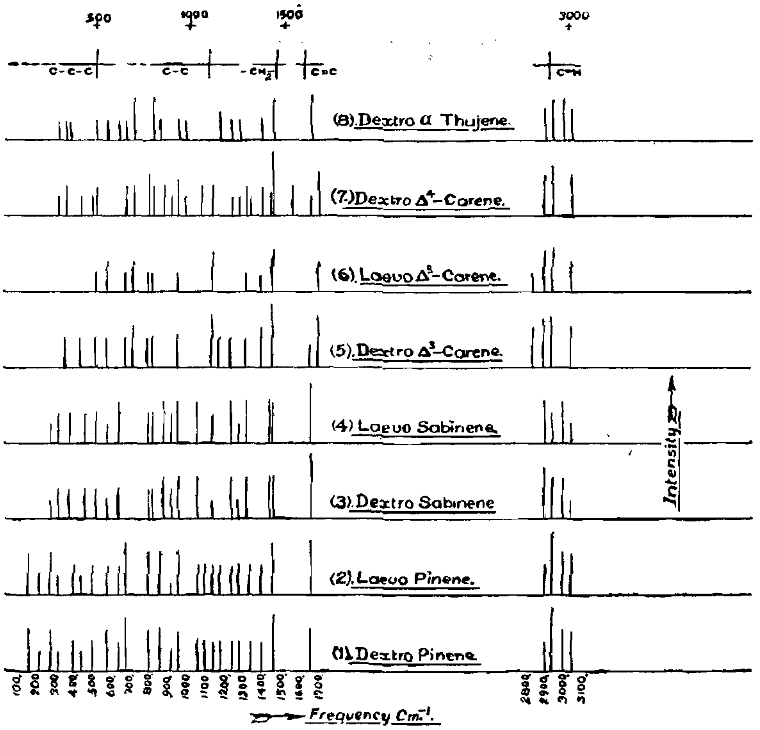

Fig. 1.

Terpenes.

TABLE I.

d.a-Pinene. α_D= 47·1		*l.a-Pinene.* α_D =44·3		*d.a-Pinene.* α_D=47·1		*l.a-Pinene.* α_D=44·3	
Authors	Infra-red*	Authors	Infra-red	Authors	Infra-red	Authors	Infra-red
145(3) (a)	..	146(3) (a)	..	1086(2) (ae)	1083	1089(2) (aeh)	..
210(1) (a)	..	208(1) (a)	..	1127(2) (e)	..	1129(2) (e)	..
265(3) (abgh)	..	264(3) (abgh)	..	1173(2) (efh)	1170	1173(2) (efh)	1170
314(1) (a)	..	314(1) (a)	..	1222(2) (ae)	1235	1223(2) (ae)	1227
396(2) (a)	..	394(1) (a)	..	1268(2) (aeg)	..	1270(2) (aeg)	..
427(1) (ag)	..	431(1) (ag)	..	1330(2) (eh)	1325	1330(2) (eh)	1325
480(2) (aefgh)	..	481(2) (afgh)	..	1381(2) (ae)	1399	1382(2) (ae)	1374
574(3) (aceg)	..	574(2) (aceg)	..	1450(4) (aefh)	..	1449(4) (aefh)	1449
626(2) (abe)	..	625(2) (abe)	..	..	..	..	1587
669(4) (aceg)	..	671(4) (aceg)	..	1658(3) (agh)	1653	1657(4) (agh)	..
..	712	..	714	..	..	..	1695
..	758	..	758	..	..	..	1733
780(3) (aeg)	787	778(3) (aeg)	..	..	..	..	1818
846(3) (aefgh)	848	849(3) (aefh)	848	..	..	..	2083
..	877	..	877	..	2128	..	..
907(1) (ae)	..	905(0) (ae)	..	..	2703	..	..
954(3) (ae)	952	953(3) (ace)	943	2881(2) (e)	..	2885(2) (de)	..
..	990	..	990	2919(5) (adeg)	2907	2917(5) (adeh)	2924
..	1010	..	1016	2993(3) (efh)	..	2992(3) (eh)	..
1044(2) (eh)	..	1046(2) (eh)	..	3030(3) (aefh)	..	3032(3) (aeh)	..
				..	..	..	3774

* W. W. Coblentz, *Investigations of Infra-red Spectra*, pp. 144-145.

TABLE II.

d.Δ_3*-Carene* $\alpha_D=9\cdot3$	*l.*Δ_3*-Carene.* $\alpha_D=2\cdot9$	*d-Sabinene.* $\alpha_D=81$	*l-Sabinene.* $\alpha_D=50$	*d.a-Thujene.* $\alpha_D=39\cdot2$	*d.*Δ_4*-Carene.* $\alpha_D=82\cdot6$
353(2) (ah)	..	(265)(1) (fg)	(264)(1) (fg)	(299)(1) (gh)	311(1) (ah)
424(2) (a)	..	316(2) (ade)	318(2) (ade)	(335)(1) (gh)	354(2) (ah)
513(2) (ah)	513(1) (h)	370(2) (a)	369(2) (a)	(372)(1) (afh)	415(1) (ae)
574(2) (aegh)	572(2) (aegh)	447(2) (a)	448(2) (a)	497(1) (abh)	485(1) (aegh)
683(2) (aegh)	684(1) (agh)	506(2) (abfgh)	500(2) (abfgh)	553(1) (agh)	517(2)(acefh)
719(3) (ae)	719(2) (ae)	569(1) (afg)	571(1) (afg)	(621)(1) (gh)	670(2) (aegh)
763(2) (ae)	760(1) (ae)	638(2) (aeh)	643(3) (aeh)	670(1) (ae)	704(2) (ae)
824(2) (aegh)	825(1) (aeh)	789(2) (ae)	788(2) (ae)	732(3) (ae)	758(3) (aeg)
939(2) (aeh)	941(1) (ae)	815(2) (aefh)	814(2) (aefh)	807(3) (aefgh)	831(2)(adegh)
1111(4) (a)	1109(3) (a)	868(3) (ae)	869(3) (ae)	843(1) (e)	862(3) (ae)
1162(2) (efh)	..	922(2) (ae)	920(2) (ae)	947(1) (aegh)	908(1) (ae)
1231(2) (e)	..	962(3) (aefh)	963(3) (aefh)	979(1) (ae)	958(3) (aeh)
1310(2) (aeh)	1312(1) (ah)	1035(3) (ae)	1037(3) (ae)	1168(2) (eh)	988(1) (e)
1372(3) (ae)	1382(1) (ae)	1112(1) (ae)	1111(2) (ae)	1210(1) (aef)	1067(2) (deg)
1437(5) (aefgh)	1439(3) (aefh)	1210(3) (ae)	1208(3) (ae)	(1274)(1) (gh)	1141(2) (e)
1641(1) (ah)	..	1273(1) (ae)	1278(1) (ae)	1382(1) (aeg)	1216(1) (e)
1683(4) (agh)	1685(2) (agh)	1310(3) (aegh)	1311(3) (aegh)	1445(3) (aefh)	1258(1) (eg)
2830(3) (eh)	2838(1) (e)	1426(3) (aeh)	1423(3) (aeh)	1642(3) (agh)	1304(2) (ae)
2877(4) (aeg)	2876(3) (ae)	1453(3) (aefh)	1456(3) (aefh)	2875(2) (aeg)	1333(1) (eh)
2920(4) (ae)	2917(3) (aef)	1652(5) (agh)	1653(5) (agh)	2910(3) (aeh)	1379(2) (aeg)
3008(2) (efh)	3008(2) (ef)	2877(4) (aeg)	2874(3) (aeg)	2980(3) (aeg)	1420(1) (e)
		2922(3) (aeg)	2924(2) (aeg)	3050(2) (efg)	1448(5) (aefh)
		2986(3) (e)	2994(3) (e)		1554(2) (a)
		3036(1) (e)	3046(1) (e)		1639(1) (ah)
					1670(3) (agh)
					2876(3) (ade)
					2918(4) (adeh)
					3005(3) (aeh)

DISCUSSION.

Frequencies due to definite bonds.

The frequencies originating from various linkages **are classified** in the following table:

TABLE III.

Raman frequencies due to different bonds.

Substance	$-CH_2-$	$C=C$	Aliphatic $C-H$	$H-C\leqslant$	$H_2C=C$
(1) *d*-Pinene ..	1450	1658	2881, 2919, 2993	3030	
(2) *l*-Pinene ..	1449	1657	2885, 2917, 2992	3032	
(3) *d*-Sabinene ..	1426 1453	1652	2877, 2922, 2986		3036
(4) *l*-Sabinene ..	1423 1456	1653	2874, 2924, 2994		3046
(5) *d*. Δ^3- Carene ..	1437	1641 1683	2830, 2877, 2920	3008	
(6) *l*. Δ^3- Carene ..	1439	1685	2838, 2876, 2917	3008	
(7) *d*. Δ^4- Carene ..	1420 1448	1554 1639 1670	2876, 2918	3005	
(8) *d*. α-Thujene ..	1445	1642	2875, 2910, 2980	3050	

In all the eight isomeric compounds, three frequencies of the C–H linkage are present with the mean values of 2875, 2915 and 2975. In the dextro and lævo Δ^3 - carenes, a smaller frequency of 2830 is also present. All the compounds except the sabinenes contain the $H-C\leqslant$ linkage which is shown by a frequency at 3025. In the sabinenes the frequency 3035 is due to the $CH_2=C$ grouping.

A frequency of the mean value of 1650, characteristic of a C=C linkage is present in all the compounds. In the dextro Δ^3 –carene and dextro Δ^4 –carene, this is split up into two and three components respectively.

The $-CH_2-$ linkage frequency of 1450 is shown by all the isomers, in some it is accompanied by a component of a smaller value.

In pinenes, the $-CH_2-$ linkage shows the rotational spectra of hydrogen around the carbon, consisting of eight sharp lines the distances of which from the 1450 line can be represented approximately by the relation given by Bonino and Cella (*Nature*, 1930, **126**, 915),

$$\Delta_v = B\,(4m - 4).$$

By putting $B = 6 \cdot 15$ and m = the even series, namely, 2, 4, 6, 8, etc., the calculated values of these rotational frequencies agree fairly well with the observed ones. Our values are in agreement with those recently reported by Bonino and Cella (*Mem. Accad. Italia Chim.*, 1931, **2**, No. 4–5–51 ; *C.A.*, 1932, **26,** 2656).

It is quite peculiar that this characteristic band in the pinenes is absent in the rest of the isomers. Recently, Bhagavantam and Venkateswaran (*loc. cit.*) have reported several faint lines in this region. These are due to sabinene which is the usual impurity in pinene. The probable explanation of the occurrence of the large number of frequencies in this region is the existence of different kinds of C–H linkages in the compounds due to the double bond as in cyclohexene, the apparent regular spacing in pinene being fortuitous.

Smaller shifts.—The very large number of frequencies in the region 200–1300 which are due to the carbon linkages, show that with increasing number of carbon atoms, spectra too complex for analysis are obtained. In a series of isomers these shifts vary owing to the changes in the structure which fact may be useful in identifying a particular compound.

TABLE IV.

Classification of frequencies of all the isomers.

d-pinene	*l*-pinene	*d*-sabinene	*l*-sabinene	*d*. Δ^3-carene	*l*. Δ^3-carene	*d*. Δ^4-carene	*d. a.*-thujene	Vibrator
139(3)	140(3)							
204(1)	202(1)							
259(3)	258(3)	258(1)	258(1)					
308(1)	308(1)	311(2)	312(2)			305(1)	292(1)	
				347(2)		348(2)	328(1)	
		364(2)	363(2)				366(1)	C-C-C
390(2)	388(2)							
421(1)	425(1)			418(2)		410(1)		
		441(2)	442(2)					
474(2)	475(2)					479(1)		
		500(2)	500(2)	507(2)	506(1)	511(2)	491(1)	
568(3)	568(2)	563(1)	565(1)	568(2)	566(2)		547(1)	
620(2)	619(2)	632(2)	637(3)				614(1)	
662(4)	665(4)			677(2)	678(1)	664(2)	664(1)	
				714(3)	713(2)	699(2)	726(3)	
774(3)	772(3)	784(2)	783(2)	757(2)	754(1)	752(3)		
		809(2)	808(2)	818(2)	819(1)	825(2)	801(3)	
840(3)	843(3)						837(1)	
		862(3)	863(3)			856(2)		
901(1)	899(0)	917(2)	915(2)			902(1)		
949(3)	948(3)	958(3)	958(3)	934(2)	935(1)	952(3)	941(1)	C-C
						982(1)	973(1)	
1038(2)	1040(2)	1030(3)	1031(3)					
1081(2)	1084(2)					1061(2)		
1121(2)	1123(2)	1107(1)	1106(2)	1106(4)	1104(3)	1135(2)		
1167(2)	1167(2)			1156(2)			1162(2)	
1217(2)	1217(2)	1205(3)	1203(3)	1225(2)		1210(1)	1204(1)	
1262(2)	1264(2)	1268(1)	1273(1)			1252(1)	1268(1)	
		1304(3)	1306(3)	1305(2)	1306(1)	1299(2)		
1324(2)	1324(2)					1327(1)		
1376(2)	1377(2)			1367(3)	1377(1)	1374(2)	1377(1)	$-CH_2-$
		1421(3)	1418(3)			1414(1)		
1445(4)	1444(4)	1449(3)	1450(3)	1432(5)	1434(3)	1442(5)	1440(3)	
						1549(2)		
1653(3)	1652(4)	1647(5)	1648(5)	1636(1)		1634(1)	1637(3)	C=C
				1678(4)	1680(2)	1665(3)		
				2825(3)	2833(1)			
2876(2)	2880(2)	2872(4)	2869(3)	2872(4)	2872(3)	2871(3)	2870(2)	
2914(5)	2912(5)	2917(3)	2917(2)	2916(4)	2912(3)	2913(4)	2905(3)	C-H
2988(3)	2986(3)	2981(3)	2989(3)				2975(3)	
3025(3)	3027(3)	3031(1)	3041(1)	3003(3)	3003(2)	3003(3)	3045(2)	

A careful study of the shifts of all the isomers shows that the frequencies 145 and 845 are characteristic of pinenes, 370 and 868 of sabinenes, 353 and 719 of Δ^3-carenes. Further the Δ^4-carene can be distinguished from the Δ^3-carenes by the presence of additional frequencies 758, 958 and 1067 in the former compound.

COMPARISON OF THE DEXTRO AND LAEVO FORMS.

The Raman frequencies of the dextro and lævo forms of the pinene and the sabinene are identical in value and also in intensity, within the limits of experimental error. The absence of some frequencies in lævo Δ^3-carene and the difference in the intensities of the frequencies of dextro and lævo forms are due to the substance lævo Δ^3-carene being not sufficiently pure. This latter fact explains the cause of faint lines obtained by Bhagavantam and Venkateswaran in lævo pinene, the commercial samples of which show rotations as low as 22°.

SUMMARY.

1. The spectra of the dextro and lævo forms of a series of isomeric terpenes are shown to be identical.

2. The structural changes among the isomers are shown in smaller shifts which may be useful in identifying these compounds in essential oils.

Our thanks are due to Dr. H. E. Watson for guidance during the course of this work.

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DETERMINATION OF CARBON IN SOILS.

By V. Subrahmanyan, Y. V. Narayanayya and (Miss) K. Bhagvat.

During recent years, several methods, direct as well as indirect, have been proposed for the estimation of carbon in soils. The direct methods which involve dry or wet combustion (Messinger, *Ber.*, 1888, **21,** 2910; Cameron and Breazeale, *J. Amer. Chem. Soc.*, 1904, **26,** 29; Salter, *Ind. Eng. Chem.*, 1916, **8,** 637; Dennstedt in Abderhalden's *Handbuch der Biologischen Arbeitsmethoden*, 1925, Abt. 1, Teil 3, 483; Winters and Smith, *Ind. Eng. Chem.* (*Anal.*), 1929, **1,** 202; Friedmann and Kendall, *J. Biol. Chem.*, 1929, **19,** 727; Heck, *Soil Sci.*, 1929, **28,** 225; Methods of Analysis, *A.O.A.C.*, 1930, 4-5; Arnold and Page, *J. Agric. Sci.*, 1930, **20,** 473; Seshadri, *Madras Agric. J.*, 1933, **21,** 413; Adams, *Ind. Eng. Chem.* (*Anal.*), 1934, **6,** 277) require special equipment and are often difficult to carry out. Some of the methods are also elaborate and time-consuming. The indirect methods, which are based on the estimation of equivalent amounts of sulphur dioxide (Robinson, McLean and Williams, *J. Agric. Sci.*, 1929, **19,** 315), chromic acid (Schollenberger, *Soil Sci.*, 1927, **24,** 65; *ibid.*, 1931, **31,** 483; Degtjareff, *ibid.*, 1930, **29,** 239; Walkley and Black, *ibid.*, 1934, **37,** 29) or permanganate (Istcherecoff, cited from Degtjareff, *loc. cit.*) are very much easier to operate and yield results of comparative accuracy when a number of specimens under similar conditions are examined. The values obtained according to those methods are not, however, quite accurate, because the underlying reactions are not specific to carbon. Thus, Bhagvat, Narayanayya and Subrahmanyan (*Proc. Ind. Acad. Sci.*, 1934, **1,** 49) have shown that in the case of soils containing appreciable amounts of chloride or ferrous iron such methods give exaggerated estimates for carbon; nor are the oxygen requirements of different organic soil components proportional to their carbon contents. Furthermore, the oxidation may not always be complete, especially when the soil contains carbon compounds like acetic acid that are not readily oxidisable Such substances are known to be formed in the swamp soils (Subrahmanyan, *J. Agric. Sci.*, 1929, **19,** 627; Bhaskaran, Narasimhamurthy, Subrahmanyan and Sundara Iyengar, *Proc. Ind. Acad. Sci.*, 1934, **1,** 155), and the failure of indirect methods to yield reliable results under such conditions, as also in presence of substances like urea, has already been pointed out (Bhagvat, Narayanayya and Subrahmanyan, *loc. cit.*). The last-mentioned authors have also studied the factors influencing the oxidation of organic matter in dry as well as swamp soils and have standardised the conditions under which complete oxidation can be ensured. Their observations have shown that (*a*) soil organic matter is far less resistant to chemical oxidation than many other forms of carbon including some apparently simple substances and (*b*) the resulting carbon dioxide is more conveniently displaced by the steam issuing from the digesting mixture than by a current of air as is usually done. The apparatus and the procedure described in the present paper are based on the findings described in the previous communication.

EXPERIMENTAL.

The Apparatus.—(Fig. 1). It consists of a Kjeldahl flask (A) (800 c.c. capacity) fitted with a rubber stopper through one hole of which passes a long-stemmed dropping funnel (B), while, through the other, passes a short tube bent at right angles connecting, through a tap (C), with the absorption system which consists of a straight condenser (D) packed with glass beads. The top of the condenser is fitted with a short-stemmed dropping funnel (E) (50 c.c. capacity) and soda lime guard tube. The lower part of the condenser is fitted, through a rubber stopper, into the receiving flask which is, preferably, a wide-mouthed, flat-bottomed flask (F) of capacity about 400 c.c.

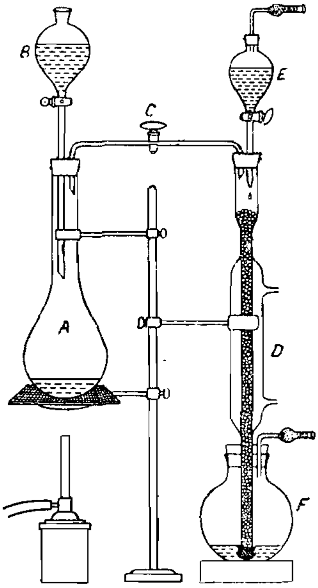

Fig. 1.

The above apparatus can be used for the estimation of carbon under a variety of conditions, only slight changes in the proportion or composition of the reagents being made to meet certain special conditions that arise in some cases. Since the previous observations (Bhagvat, Narayanayya and Subrahmanyan, *loc. cit.*) have shown that the oxidation proceeds rapidly to completion and that the vapours which pass over up to a late stage are exclusively steam and carbon dioxide, it is not considered necessary either to supplement the oxidation by additional equipment or to interpose traps to absorb acid fumes and other vapours which may interfere with the estimation of carbon dioxide.

Estimation of total carbon in dry soil.—The specimen is ground to fine powder passing the 100–mesh sieve and a known weight (5–10 g.) introduced into the Kjeldahl flask either in the dry condition or as suspension in water or alkali. It should be ordinarily possible to obtain accurate estimates upto a total of 200 mg. of carbon and, reckoning on that basis, it would be rarely necessary to take less than 5 g. of soil while, in many cases, especially when the specimens are of tropical origin, very much larger quantities, ranging from 20-25 g., can be conveniently handled. Pure, finely powdered potassium dichromate (10-15 g.) is then introduced and the sides of the flask washed down with distilled water, care being taken that the total quantity of water including that originally present does not exceed 25–30 c.c. The aqueous suspension is then shaken vigorously so as to break up any lumps that may have been formed. The flask is then stoppered and clamped in position.

The absorption system is prepared by pipetting out an excess (50-60 c.c.) of 2–4 N carbonate-free potassium hydroxide into the dropping funnel (E). About 10 c.c. of the alkali is first allowed to trickle down the condenser into the receiving flask (F). The remaining quantity is then let in drop by drop, the rate being so regulated that the alkali continues to trickle through the column of glass beads throughout the period of heating which is about 20 minutes.

A measured quantity (30–40 c.c.) of concentrated sulphuric acid is introduced into the long-stemmed dropping funnel (B). The tap is opened and the acid allowed to flow along the sides of the flask. Most soils require only 15–20 c.c. of acid for complete digestion, but there are, nevertheless, some (especially those rich in iron and alumina) which require more—hence the need for a larger quantity. It is not always possible to introduce the acid by merely opening the tap. In some cases, especially those of soils containing fairly large amounts of carbonates, there is vigorous gas production as soon as the first few c.c. of acid are added, so that, if sufficient care is not taken, a part of the carbon dioxide may escape upward, through the column of acid. A convenient procedure would, therefore, be to blow in the acid using a one-holed stopper fitted with a bent glass tube and rubber extension for the purpose. The blowing should be done in instalments and the tap closed from time to time so that there may not be too rapid a rush of gas into the absorption system. A small quantity (1–2 c.c.) of acid should be allowed to remain in the dropping funnel so as to act as seal against the carbon dioxide of the air being blown in. If there is no immediate action, the contents of the flask may be mixed together by gentle rotation and heated with a low flame in the initial stages. Bhagvat, Narayanayya and Subrahmanyan (*loc. cit.*) have shown that the most rapid evolution of carbon dioxide is between 5 and 10 minutes after commencement of heating—just before and for some time after steam begins to condense in the absorption system. If, during this period, the heating is carried out carefully, the gas passes over at a steady rate into the condenser where the large surface presented by the glass beads moistened with trickling alkali combined with the cooling serves as a very efficient absorbent system. The steam evolved from the digesting mixture displaces the last traces of carbon dioxide from the Kjeldahl flask. As the vapours get cooled in the condenser, there is fall in pressure in that section of the apparatus, so that the alkali from the receiving flask (F) rises to some extent in the condenser thus constituting an effective seal through which no carbon dioxide can escape. After steam has thus condensed for about 5 minutes, the flame can be raised and the heating continued vigorously for a further period till the oxidation is complete. The latter stage (which will ordinarily be reached in about 15 minutes after steam begins to issue) is indicated by the precipitation of the deep red chromium trioxide followed by its decomposition resulting in the evolution of oxygen. There will also be marked swelling of the digesting mass accompanied by steady change in colour (from red to green), through various stages. All the above-mentioned changes are well defined and as they continue over several minutes, serve as unmistakable indications of the stage at which the distillation ought to be stopped.

When the oxidation is complete, the central tap (C) is turned off, disconnecting the absorption system from the remaining part of the apparatus and immediately following that, the tap of the funnel (B) is fully opened to equalise pressure inside the Kjeldahl flask. The small quantity of alkali left in dropping funnel (E) is then run in rapidly and washed with about 200 c.c. of distilled water added in lots of 30–40 c.c. at a time. From time to time a few drops of phenolphthalein are run in to verify the complete removal of the last traces of any alkali that may be adhering to the glass beads. The absorption flask (F) is now disconnected after washing into it any alkali that may be adhering to the lower parts of the condenser as also to the copper gauze tied at the bottom. Barium chloride (10 c.c., 10 per cent.) is next added to the contents of F to precipitate the carbonate, and the unused alkali titrated against standard hydrochloric acid (2–3 N) to phenolphthalein end point. During titration, the flask must be continuously shaken with a rotatory motion and the acid let in slowly ; otherwise, the concentration of the acid may become localised, resulting in the precipitated carbonate being acted on. It is desirable to finish the titration against 0·1–0·2 N acid so that the error of titration may be greatly reduced.

If pure alkali is used for absorption and the distillation stopped at the proper stage, the suspension left after titration should yield a clear solution on addition of a few drops of concentrated hydrochloric acid. The test would generally provide a useful indication of the accuracy of the procedure in each experiment. The persistence of even slight turbidity would ordinarily indicate the presence of sulphate and suggest that acid fumes had passed over. Correction for carbon dioxide present in the apparatus and reagents and that absorbed from the air during the titration is generally negligible, but it would, nevertheless, be desirable to carry out, from time to time, a blank distillation with only dichromate and sulphuric acid (1 : 1) and absorbing the vapours in standard alkali in the usual way.

Calculation of the carbon content is comparatively simple. 1 c.c. of normal alkali corresponds to 6 mg. of carbon and reckoning on the volume and strength of the alkali used up and the weight of soil taken, the percentage of carbon in the soil can be easily computed.

Estimation of carbon in some representative specimens of Indian soils.—Air-dry samples (10 g.) were analysed according to the procedure outlined above. The values thus obtained were compared with those secured by (*a*) calculation from loss on ignition by applying the usual factor and (*b*) dry combustion. The results have been presented in Table I.

TABLE I.

Description	PERCENTAGES				
	Moisture	Loss on ignition	Total carbon by		
			Wet combustion (new method)	Dry combustion	Calculation—$\frac{\text{Loss on ignition}}{1{\cdot}724}$
Paddy soil from Burma	6·1	4·67	0·52	0·55	2·71
Rain-fed soil from Punjab	2·0	2·79	0·46	0·46	1·62
Sandy soil from Ceylon	0·6	1·20	0·27	0·29	0·70
Upland soil from South Bihar	4·0	2·95	0·51	0·50	1·71
Laterite soil from Bangalore	2·2	4·54	0·72	0·71	2·64
Peaty soil from Travancore	5·6	41·56	12·40	....	24·11
Alluvial soil from Godavari Delta	8·1	5·32	0·85	....	3·09
Alkali soil from Sindh	2·4	5·85	1·42	....	3·39

.... Not determined.

It may be noted that there is close agreement between values obtained by the new method and by dry combustion while those calculated from loss on ignition are very much higher. Since the latter include combined water and volatile mineral constituents, the results obtained by that method are hardly reliable. They do not bear even an approximate relation to the values obtained by the two combustion methods.

Estimation of carbon in swamp soils.—Evidence has already been adduced to show that (*a*) incomplete oxidation of organic matter associated with the swamp soil is due partly to the resistance and partly to the volatility of some of the products associated therewith and (*b*) increasing the proportion of acid to water leads to improvement in the efficiency of oxidation while addition of different dehydrants or mineral catalysts is without any effect (Bhagvat, Narayanayya and Subrahmanyan, *loc. cit.*). The procedure for the estimation of carbon in the swamp soil would therefore be the same as the one already described except that at least 50–60 c.c. of concentrated sulphuric acid should be used for digesting 25–30 c.c. of soil suspension. The following results obtained for three specimens of soil containing known quantities of acetic acid would show that quite accurate results can be obtained according to this procedure:—(1) total carbon expected (in mg.), 174·0; found, 174·1; (2) expected, 136·0; found, 136·0; (3) expected; 130·1; found, 130·0.

Estimation of total carbon in presence of chlorides.—Most soils contain only minute quantities of chlorides, so that the correction for the alkali taken up by the chlorine or hydrochloric acid passing over into the absorption system would be generally negligible. In the case of alkali soils, however, and especially in those which are also poor in carbon, the error due to chlorides is considerable and should therefore be either eliminated altogether or the necessary correction applied to the titre values.

Cameron and Breazeale (*loc. cit.*) have drawn attention to the fact that the error due to the presence of small amounts of chloride can be eliminated by running in chromic acid cautiously and not heating the acidulated mixture until the reaction has proceeded for some time. They also suggest that if the quantity of chloride is relatively large, the soil may first be heated on the water-bath with dilute sulphuric acid until the major part of it is removed as hydrochloric acid. It is not ordinarily possible, however, to determine whether a soil is rich or poor in chlorides without conducting an analysis. In many cases, there is no visible reaction in the early stages, so it would be difficult to ascertain when the digestion should be commenced. Heating the soil with sulphuric acid, however dilute, is also undesirable, because, in addition to carbonate carbon, some organic carbon may also be thereby lost. It was considered necessary, therefore, to either completely eliminate the error due to chlorides or find an easy method of applying correction for such quantities as may pass over during the experiment. Some experiments were first carried out by fitting within the Kjeldahl flask a bulb trap containing glass beads moistened with silver sulphate so that the vapours will have to pass through it before entering the absorption system. The results obtained for parallel samples of a soil to which known quantities of chlorides were added have been presented in Table II.

TABLE II.

Chloride (as NaCl) per cent.	Total carbon as estimated (in mg.)
Nil (control)	36·0
0·2	36·0
0·5	36·1
1·0	36·5
2·0	37·3

It may be seen from the above that the trap was efficient only when the chlorides were under 0·5 per cent. It cannot therefore be relied upon for the estimation of carbon in alkali soils which often contain higher percentages of chlorides.

Attempts were next made to apply correction for the chlorine and hydrochloric acid passing into the absorption system. Free chlorine was estimated iodimetrically and total chloride by precipitation methods in both neutral and acid media. When known quantities of alkali chlorides were added to the soil, it was found that a part of the chlorine always remained behind in the Kjeldahl flask while the rest passed over as mixtures of chlorine and hydrochloric acid. Thus, in one experiment, out of 60 mg. of total chlorine (added as chloride), 38·5 mg. passed over in the elementary form and 9·5 mg. as hydrochloric acid while the rest (12·0 mg.) remained behind in the digestion flask.

It was noted that in most of the experiments, accurate estimates of carbon could not be obtained even after applying correction for the chlorine which had passed over. The values were generally discordant. Thus, in the case of a specimen of Bangalore soil, they ranged from 0·67 to 0·86 per cent. In view of these discrepancies, that procedure was given up as unsatisfactory.

Some experiments were next carried out adding excess of silver sulphate directly to the contents of the Kjeldahl flask instead of introducing it into the trap. It was then observed that there was not even a trace of chloride in the distillate, thereby suggesting that silver chloride which was presumably first formed was not acted on by sulphuric acid under the conditions of the experiment. It also appeared probable that addition of salts of other metals, especially those forming insoluble or, at any rate, sparingly soluble chlorides, may similarly arrest the formation of chlorine and hydrochloric acid. Some trials were therefore carried out adding 10 c.c. of 1 per cent. sodium chloride to 5 g. lots of a specimen of soil which was originally free from chlorides. After adding 5 g. of one of the sulphates mentioned below and 10–15 c.c. of water, the suspensions were digested with dichromate and sulphuric acid in the usual way (Table III).

TABLE III.

Treatment	Carbon (as estimated) in mg.	
	I	II
Soil alone (control) ..	36·0	36·0
,, + NaCl	38·7	37·2
,, + ,, + $CuSO_4$ (anhydrous) ..	37·5	38·5
,, + ,, + $PbSO_4$ ..	36·9	37·2
,, + ,, + $HgSO_4$ ..	36·0	36·0
,, + ,, + Ag_2SO_4 ..	36·0	36·0

The sulphates of copper and lead were not effective while those of mercury and silver were highly efficient and yielded the same results as the control.

The experiments were next repeated, varying the proportion of chloride to correspond to 0·5, 1·0, 2·0 and 5·0 per cents. respectively on the weight of the soil. The proportion of sulphuric acid to soil suspension was also increased so as to correspond to double or triple the usual quantity. In all the cases, the error due to chlorides was entirely eliminated by adding 5 g. of either silver or mercuric sulphate. These observations show that the treatment can be applied to all types of soils including those under swamp conditions.

In view of the recent observations of Krough and Keys (*Biol. Bull.*, 1934, **67**, 132) on the elimination of error due to chlorides in sea water, some trials were carried out adding thallium sulphate in sufficient quantity to precipitate all the chloride and then conducting the digestion in the usual way. The estimates thus obtained were, however, of the same order as those with copper or lead sulphate, thereby showing that the treatment is not applicable to soils.

Since silver salts are very costly and therefore not suitable for routine operations, the studies were next directed to the standardisation of conditions for the use of a mercury salt for the purpose. The trials were carried out with different concentrations of chlorides and varying quantities of metallic mercury, mercuric oxide or mercuric sulphate. The results have been presented in Table IV.

TABLE IV.

Form of mercury	Percentage of chloride in the soil (as added)	Quantity (in g.) of mercury (free or combined) added to 5 g. of soil		
		1·0	2.0	5.0
		Total carbon as estimated (in mg.)		
Mercury (metal)	0·5	42·9	43·4	44·0
	1·0	43·5	44·0	44·4
	2·0	44·2	44·6	44·4
Mercuric oxide (red)	0·5	42·5	42·5	42·5
	1·0	42·6	42·5	42·5
	2·0	42·8	42·6	42·5
Mercuric sulphate	0·5	42.5	42·5	42·5
	1·0	42·7	42·5	42·5
	2·0	42·8	42·6	42·6

Total carbon in untreated soil (control)—42·5 mg.

It was noted that in addition to yielding unsatisfactory results, addition of metallic mercury also rendered the digestion very difficult. The heavy pellet settled at the bottom and caused violent bumping. As the result of this, there was a tendency for the acid digest to shoot up in the Kjeldahl flask, so that there was also the danger of a part of the acid being mechanically carried over into the absorption system. In presence of the oxide or the sulphate, the digestion proceeded smoothly and, as will be seen from the results, the error due to chlorides (allowing for small experimental differences) was entirely eliminated when quantities equivalent to 2–5 g. of mercury were added.

The above experiment was next repeated with different soils and increasing concentrations of chloride upto 20 per cent. It was observed that although in the case of certain soils—especially those of the laterite or red gravel type which are rich in iron and alumina—addition of 10 g. of mercuric oxide was effective in completely eliminating the error, it was only partially so in other cases. It was noted, however, that any quantity upto 10 per cent. of chlorides can be easily dealt with in all the cases irrespective of the nature of the soil. Since most alkali soils of the world contain well under 5 per cent. of chlorides, it may be safely assumed therefore that by adding 5 g. of mercuric oxide to the digesting mixture, the error due to chlorides can be entirely avoided.

The mechanism of the action of mercury or silver in checking the formation of chlorine is still obscure, but the following observations may be of interest:—(*a*) whether in aqueous solution or admixed with soil suspension, alkali chlorides are readily attacked by the oxidising mixture; (*b*) when present by itself chloride of mercury or silver is not resistant, but when mixed with the soil, it does not yield even a trace of hydrochloric acid until long after the complete oxidation of carbon; (*c*) alkali chloride to which excess of mercury or silver salt is added is not resistant in presence of water alone; when combined with the soil, it withstands the action of the oxidising mixture in the same manner as silver or mercuric chloride does. These observations would show that the elimination of error is due to the combined action of silver or mercury and certain constituents of the soil.

Since the retention of chlorine was most prominent in soils which were rich in iron and aluminium oxides, it appeared probable that either or both of those mineral constituents might have contributed to such action. With a view to determining whether they could, by themselves, produce the same effect, some experiments were carried out adding 2, 5 and 10 g. respectively of either of those substances to suspensions containing 5 g. lots of quartz powder together with 10 c.c. of 1 per cent. sodium chloride. The results showed, however, that varying quantities of chlorine and hydrochloric acid had passed over in all the cases. The experiments were next repeated adding silver or mercuric sulphate (5 g.) together with iron or aluminium oxide or laterite to the solution of chloride. It was observed that appreciable quantities of chlorine and hydrochloric acid were still passing over. These observations would show that the mechanism of retention of chlorine by the soil is more complicated than it first appeared. Further work is needed to throw light on this aspect of the problem.

Total carbon in presence of nitrates.—Since most soils contain nitrates—though generally only in minute quantities—it appeared probable that treatment with the oxidising mixture would lead to the production of nitric acid and different oxides of nitrogen which might pass over and thus affect the accuracy of the estimate of carbon. With a view to obtaining an idea of the error which may thus be introduced, the following experiments were carried out:—To 5 g. lots of a specimen of black cotton soil (from Nagpur) sodium nitrate was added in quantities corresponding to 200, 400 and 600 parts per million and the suspensions (25 c.c.) oxidised in the usual way with 5 g. of dichromate and 30 c.c. of sulphuric acid. In another set of trials, the oxidations were repeated using double the quantity (60 c.c.) of sulphuric acid. In a third set, the soil suspensions were treated with 2 g. each of mercuric oxide together with dichromate and acid.

It was noted that, in all the cases, correct estimates of carbon (0·97 per cent.) were obtained. Since the nitrate contents of field soils are generally very much less than those added in the previous experiment, it may be inferred that soil nitrates do not interfere with the accuracy of the estimation of carbon by wet combustion.

The foregoing observations should not be taken to mean that there is no reaction at all between nitrates and sulphuric acid under the conditions of digestion for carbon. Traces of nitrous vapours do indeed pass over, but they do not affect the titre value. In fact, even if the entire quantity of added nitrate had been acted on, the resulting acid would not have corresponded to more than one drop of Normal alkali.

Carbonates and organic carbon: Dry soil conditions.—Several methods have been proposed for the estimation of carbonates in soils and some of them are known to give accurate values (Hall and Russell, *J.C.S.*, 1902, **81,** 81; Amos, *J. Agric. Sci.*, 1905, **1,** 322; Collins, *J. Soc. Chem. Ind.*, 1906, **25,** 518; Hutchinson, *J. Agric. Sci.*, 1914, **6,** 323; MacIntire and Willis, *Ind. Eng. Chem.*, 1915, **7,** 227). Since it is desirable, however, that the same equipment should serve for the estimation of both carbonates and organic carbon, some experiments were carried out with the apparatus described in an earlier section of the paper.

To samples (5 g.) of a Bangalore soil (which was free from carbonates), known quantities of alkali carbonate (in solution) were added and the suspensions (25 c.c.) treated with 40 c.c. each of 1 : 15 solution of hydrochloric, sulphuric or phosphoric acid. They were then raised to boiling and the vapours received in the absorption system in the usual way. Since there was no definite end-point as in the case of total carbon, the distillations were stopped at the end of 30 minutes, the rate of heating being so adjusted that a third of the added water was still left in the flask. The carbon contents, as determined by back titration, showed that there was complete recovery of the added carbonate in all the cases.

The foregoing observations having shown that there is no danger of acid vapours passing over under the conditions of the experiment, the trials were next extended to certain soils which were known to contain carbonates. The soil suspensions (5 g. in 25 c.c.) were treated in the same manner as in the previous experiment and the distillations stopped at the end of 10, 20 and 30 minutes respectively, the rates of distillation being so regulated that about one-third, half and two-thirds respectively of the added water had distilled over at the time of stopping the heating. The estimates of carbon thus obtained have been presented in Table V.

TABLE V.

Acid used	Time of boiling in minutes	Carbonate as mg. of carbon in soil from		
		Sindh	Mandya	Tindivanam
Hydrochloric (40 c.c., 1 : 15)	10	49·5	21·8	6·8
	20	49·5	21·8	6·8
	30	49·5	21·8	6·8
Sulphuric (40 c.c., 1 : 15)	10	49·5	21·8	6·8
	20	49·5	21·8	6·8
	30	49·5	21·8	6·8
Phosphoric (40 c.c., 1 : 15)	10	49·5	21·7	6·4
	20	49·5	21·8	6·8
	30	49·5	21·8	6·8
Boric (5 g. + 40 c.c. water)	10	13·7	6·5	3·2
	20	13·7	6·5	3·2
	30	13·7	6·5	3·2

It may be seen from the above that boiling for even 10 mins. was sufficient to displace all the carbon dioxide from specimens treated with hydrochloric or sulphuric acid. Those treated with phosphoric acid yielded correct estimates only after boiling for twenty mins. Specimens which were boiled with boric acid yielded consistently low values even after 30 minutes.

Although concordant values were obtained for the particular specimens of soil that were used in the above study, it was yet realised that in presence of calcium salts, sulphuric or phosphoric acid may not prove so useful as hydrochloric acid Such was indeed the case when the carbonate content of the soil mixed with a known quantity of chalk was estimated. The specimen treated with dilute hydrochloric acid yielded the correct value (96 mg.) while that treated with sulphuric acid yielded an estimate of only 81 mg. even after prolonged boiling.

The volatile character of hydrochloric acid would no doubt restrict the range of concentration within which it can usefully be employed. It is fortunate, however, that only very dilute acid (about 2·5 per cent.) is required for the decomposition of carbonates. As the result of reaction with the carbonate, as also with the mineral constituents of the soil, the strength of the acid is further reduced so that there is practically no danger of any of it passing into the distillate during the first half hour. The reaction between carbonate and acid is almost instantaneous and since the previous observations have shown that boiling for even 10 minutes is sufficient to displace all the resulting gas, it may be concluded that by stopping the distillation at a fairly early stage, the error due to acid vapours may be entirely avoided.

It should be admitted, however, that the use of hydrochloric acid for the estimation of carbonates would interfere with the determination of organic carbon in the residue. The volume and the concentration of the added acid would be so considerable that large quantities of mercury or silver salts would be required to check the acid vapours. It is doubtful if, even then, it would be effective in all soils. It may be necessary therefore to determine total carbon on a separate sample and to estimate organic carbon by difference. This duplication of procedure can be avoided if the nature of the soil can be ascertained beforehand, so that if it is not rich in lime, sulphuric or phosphoric acid may be used for the estimation of carbonates. In such cases, there will be no difficulty in digesting the residue for organic carbon.

Attention has already been drawn to the fact that the estimate of carbonate carbon is not affected even if the distillation is continued over several minutes. It was not clear, however, if the organic carbon remains unaffected by such a treatment. Thus, it appeared probable that certain non-acid, volatile, carbon compounds may pass over into the distillate and thus escape detection. With a view to determining whether such changes occur at all, the estimations of organic carbon were carried out by two methods,—(1) directly on the residue left after decomposition of carbonates, and (2) indirectly, by estimating total carbon and subtracting the value obtained for carbonate. The two sets of results thus obtained have been presented in Table VI. For reasons already stated, hydrochloric acid was not used for the direct estimation.

It may be seen from the table that both the methods yield the same values, thereby showing that none of the organic carbon is lost during boiling with dilute mineral acid. The higher estimates obtained as the result of treatment with boric acid are fictitious since they include unattacked carbonate.

TABLE VI.

Acid used for decomposing the carbonate	Organic Carbon (in mg.) by					
	Direct Method			Indirect Method		
	Soil from			Soil from		
	Sindh	Mandya	Tindivanam	Sindh	Mandya	Tindivanam
Sulphuric or Phosphoric	23·0	9·9	7·7	23·0	9·9	7·7
Hydrochloric ..	..	..	..	23·0	9·9	7·7
Boric	58·8	25·2	11·3	58·8	25·2	11·3

Carbonate and organic carbon in swamp soils.—This estimation is rendered difficult by the presence of free as well as combined fatty acids which yield acid vapours when the soil is boiled with dilute mineral acid. With a view to eliminating this source of error, some experiments were carried out treating the soil first with carbonate-free sodium hydroxide to render it alkaline and then with excess of barium chloride solution to precipitate all the carbonate. The suspension was then filtered and washed frequently with carbon dioxide-free water. The wet precipitate was transferred to the Kjeldahl flask together with the filter paper and the carbonate estimated in the usual way by treatment with excess of dilute hydrochloric acid.

It was expected that the barium salt of fatty acids being soluble, or at any rate, very much more so than the carbonate, would be washed away leaving only the carbonate and a part of the organic carbon on the filter. The estimates obtained according to the above-mentioned procedure for soil suspensions to which known quantities of carbonates and acetates had been added were compared with the quantities actually expected. The values for organic carbon were also obtained by the indirect method and compared with the expected values (Table VII).

The results show clearly that the procedure outlined above is quite reliable for the estimation of carbonate and organic carbon under swamp soil conditions.

Estimation of different forms of carbon in a soil of unknown composition: A general procedure for all soils.—It is not always possible to trace the previous history of soils under examination or to conduct preliminary analyses with a view to determining the composition and proportion of the reagents to be employed in each case. It would be desirable therefore to adopt a simple procedure that could be applied to all soils irrespective of their composition. Since the different modifications developed in the present paper are more or less additive

TABLE VII.

Composition of suspension	Carbonate as mg. of carbon		Organic carbon as mg. of carbon	
	Calculated	Found	Calculated	Found
Paddy soil (10 g.) + sodium acetate (10 c.c., 1 per cent.) + sodium carbonate (20 c.c., 1 per cent.)	22·6	22·7	52·7	52·7
Paddy soil (10 g.) + sodium acetate (10 c.c., 1 per cent.) + sodium carbonate (40 c.c., 1 per cent.)	45·2	45·0	52·7	52·6
Paddy soil (10 g.) + sodium acetate (20 c.c., 1 per cent.) + sodium carbonate (20 c.c., 1 per cent.)	22·6	22·6	82·0	82·0
Paddy soil (10 g.) + sodium acetate (20 c.c., 1 per cent.) + sodium carbonate (40 c.c., 1 per cent.)	45·2	45·2	82·0	82·0

in character and do not interfere with each other, a convenient procedure would be to assume that the soil under examination may contain some resistant organic substances like urea, volatile acid products, chlorides, nitrates and carbonates and treat it in such a manner as would yield accurate estimates in presence of all these products. A comprehensive procedure for the estimation of total carbon would be as follows.—The soil suspension (5 g. in 25 c.c.) is treated with 10 g. dichromate, 5 g. of mercuric oxide and slightly more than double the volume of concentrated sulphuric acid as that of the water in the medium. The digestion, absorption of vapours and back titration of unused alkali are then conducted in the usual way.

The estimation of carbonates may, in a like manner, be carried out on the assumption that volatile acid products would be formed on boiling the soil suspension with dilute mineral acid. The treatment for eliminating this source of error would be the same as that described for the swamp soil. Since treatment with alkali and subsequent washing may remove some of the soil organic matter together with the salts of fatty acids, estimation of organic carbon on the residue left after decomposition of carbonates would not yield accurate values. A satisfactory procedure will be to take two separate samples of soil or soil suspension and to determine total carbon on the one and carbonate on the other. The difference between the two estimates would be the value for organic carbon.

DISCUSSION.

The results of the present enquiry, as also those of the previous one (Bhagvat, Narayarayya and Subrahmanyan, *loc. cit.*) have brought into relief a number of interesting features relating to wet oxidation of organic matter in soils. Not only is the oxidation very rapid, but the type of equipment required for carrying it out is also quite simple. A considerable part of the complicated apparatus adopted by previous investigators has been eliminated, and the remaining part so adjusted that both the displacement of the vapours and the absorption of carbon dioxide have been rendered more efficient. The appendage of traps for different types of acid vapours is also done away with and the related errors eliminated by simple modifications in the composition and proportion of the digesting mixture. The procedure for estimation has been rendered so simple, and the details of manipulation so easy to follow that the determination can now be carried out as a routine operation. The whole estimation takes only about 20 minutes and if provided with three or four sets of apparatus, a single investigator can complete 15 to 20 determinations in the course of a working day. The equipment being compact, the chances of error through leakage or otherwise are also small, so that it should be possible for an experienced worker to obtain carbon estimates which would be correct to the first decimal place and very nearly agree in the second if reckoned on the usual percentage basis.

A further feature of interest about the present method is that it takes into account all types of soil conditions, including some new ones which are of considerable practical interest but have not been considered by any of the previous investigators. This would naturally extend its application not only in routine practice but also in researches having a bearing on carbon transformations in soils.

Although the present research relates primarily to standardisation of conditions for the estimation of soil carbon, the various observations would suggest that it can be easily extended to all organic substances in general. Attention has already been drawn (Bhagvat, Narayanayya and Subrahmanyan, *loc. cit.*) to the fact that the method yields accurate estimates when applied to pure organic substances. It can deal with fairly large quantities of substances so that the experimental error can be greatly reduced. The estimations can also be easily replicated, so that, by carrying out a number of parallel estimations, the error of the mean can be lowered to a minimum.

The method can also be applied to different biological products which do not easily permit of drying and those which offer considerable difficulty in handling. The extension of the technique would, in fact, open a vast line of research on various carbon transformations and economy of carbon, in general, in different types of living tissues whether of animal, plant or microbial origin. The procedure for such estimations would be similar to that described in the present paper though slight modifications with regard to details such as collection and storage of sample, quantities to be treated and such like will have to be introduced to suit the types of materials under investigation. It is hoped that the study of these and related aspects of the problem would form the subjects of later communications.

It is generally believed that the end product of sulphuric acid digestion of any nitrogenous substance (with the exception of the nitrate) is ammonia, which would be retained as the corresponding salt. It is reasonable therefore to expect that the residue after wet combustion would be suitable (or, at any rate, very nearly so) for distillation with alkali as in the Kjeldahl method. The experience of previous workers in this direction has, however, been discordant. Some state that the residue after oxidation of carbon yields correct values for nitrogen, while others point out that it is not suitable and requires further digestion prior to distillation of ammonia (Anderson, *J. Biol. Chem.*, 1924, **61**, 57; Brown, *Ind. Eng. Chem.*, 1927, **19**, 629; Adams, *loc. cit.*).

A number of experiments carried out by the present authors would show that (*a*) the residue after oxidation of carbon yields low estimates of nitrogen when distilled, as such, with excess of alkali, (*b*) further digestion conducted, as in the usual Kjeldahl method, improves the value, but a part of the nitrogen still remains unattacked, and (*c*) the incomplete digestion is traceable to the presence of large quantities of chromium salts in the medium. The following results (Table VIII) obtained from three typical soils would illustrate the above.

TABLE VIII.

Description of soil	Nitrogen per cent. as estimated by	
	Improved Kjeldahl method*	Digestion of residue after estimation of carbon
Red sandy loam—Bangalore ..	0·078	0·072
Kalar (alkali) soil—Sindh ..	0·060	0·050
Black cotton soil—Nagpur ..	0·070	0·065

* Sreenivasan and Subrahmanyan, *Indian J. Agric. Sci.*, 1933, **3**, 646.

Similar low yields were also obtained in the case of yeast. The mechanism of retention of nitrogen is still obscure, but there is evidence to show that (*a*) as the quantity of chromium is increased (either by using more dichromate for oxidation of carbon or by adding chromium salt to the digesting mixture), larger amounts of nitrogen are retained, and (*b*) the undigested nitrogen is in combination with the insoluble residue, the main constituent of which is chromium (Cr_2O_3 ?). Further work on these and allied problems is in progress and will form the subject of a later communication.

SUMMARY.

1. A simple and elegant piece of apparatus for the wet combustion of soils has been described. Its special features are (*a*) elimination of the usual equipment for aeration, (*b*) improved efficiency in the absorption of carbon dioxide, (*c*) elimination of traps for absorbing chlorine and other acid vapours, and (*d*) adaptability for all types and conditions of soils.

2. The procedure for the estimation of carbon in dry soils has been outlined. The results, which have been compared with those obtained by dry combustion, show that the method is highly reliable.

3. Complete oxidation of the organic constituents of the swamp soil can be ensured by adjusting the volume of concentrated sulphuric acid so as to correspond to at least twice that of the water in the soil suspension.

4. When the soil contains chlorides, it is not possible to obtain accurate estimates of carbon by merely applying correction for the chlorine and hydrochloric acid which pass over. The error can be entirely eliminated, however, by adding silver sulphate, mercuric sulphate or mercuric oxide to the digesting mixture. The related conditions have been standardised.

5. Even abnormally large quantities (600 parts per million) of nitrates do not interfere with the accuracy of the estimate of carbon.

6. Using the same apparatus, the conditions for the estimation of carbonates in dry as well as swamp soils have been standardised. Dilute solutions of hydrochloric, sulphuric or phosphoric acids are equally efficient in most cases, but when the soil is rich in lime, hydrochloric acid yields the most accurate results. In the case of the swamp soil, addition of baryta followed by washing the precipitate on the filter removes the volatile fatty acids which interfere with the estimation. On distillation with excess of hydrochloric acid, the residue yields the correct estimate for carbonate including dissolved carbon dioxide.

7. A comprehensive procedure for the estimation of total and organic carbon in any type of soil has been outlined.

8. The application of the method for the estimation of carbon in different types of biological products and organic substances in general has been indicated.

9. Even after prolonged digestion, the residue left after oxidation of carbon does not yield correct estimates for total nitrogen. The defect is traceable to the presence of large quantities of chromium salts in the digesting mixture. The unattacked nitrogen is present in combination with the precipitate formed during digestion.

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ON ATMOSPHERICS AT BANGALORE DURING THE POLAR YEAR.

By S. P. Chakravarti and B. H. Paranjpye.

1. INTRODUCTION.

Atmospherics or electromagnetic disturbances of the atmosphere have been studied on long and short wavelengths by a number of investigators[*] in different parts of the world, for a knowledge of their origin and characteristics is of great value for determining the best measures to be adopted to minimise their effects on radio reception and supplying information for weather forecasting on account of their close relation to meteorological conditions.

The work of these investigators has been mainly restricted to observations in temperate climates and can therefore give little information regarding atmospherics in the tropics. In India atmospheric disturbances are prevalent throughout the year. In certain months they are so severe that radio reception is practically impossible, while in other months they are tolerable. As far as the authors' information goes, no work relating to observations in this country has yet been published and it was therefore considered desirable to undertake similar studies in this climate and to compare the results with those obtained elsewhere.

The following lines of investigation have been mainly followed by the previous investigators:—

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[*] Wilson, *Proc. Royal Society*, **92,** 555, 1916.

Watt and Appleton, *Proc. Royal Society*, **103,** 84, 1923.

Round, Eckersley, Tremellen and Lunnon, *Journal Inst. Elec. Engrs.*, **63,** 933, 1925.

Watt and Herd, *Journal Inst. Elec. Engrs.*, **64,** 611, 1926.

Watt, *Journal Inst. Elec. Engrs.*, **64,** 596, 1926.

Appleton, Watt and Herd, *Proc. Royal Society*, **111,** 615, 1926.

Cairns, *Proc. Inst. Radio Engrs.*, **15,** 985, 1927.

Austin, *Proc. Inst. Radio Engrs.*, **15,** 837, 1927.

Armstrong, *Proc. Inst. Radio Engrs.*, **16,** 15, 1928.

Potter, *Proc. Inst. Radio Engrs.*, **19,** 1731, 1931.

Potter, *Proc. Inst. Radio Engrs.*, **20,** 1512, 1932.

Munro and Huxley, Radio Research Board, Australia, 1932, *Report* No. 5.

(i) Determination of the direction of arrival of the atmospherics and location of their sources.

(ii) Examination of the wave-form of atmospherics.

(iii) Determination of the number of atmospherics per minute.

(iv) Determination of the distribution of noise due to atmospherics in long and short wave bands.

The present paper relates to observations recorded at Bangalore (12°58′ North and 77°38′ East) in response to the request of the International Polar Year Sub-Commission for such measurements being carried out at the Indian Institute of Science during the Second International Polar Year, extending from 1st August 1932 to 31st August 1933. In the absence of any definite instructions in the matter in August 1932, it was originally intended to record the observations on 15 kc/s. (20 Kms.) and this was the wavelength used up to 21st November 1932. However, subsequently, on receipt of information from the Polar Year Sub-Commission to the effect that it would be preferable to carry out the recording on 27 kc/s. (11·11 Kms.) in order to make the observations comparable with those made elsewhere, this latter wavelength was used after 21st November 1932.

The investigation comprises (*a*) the determination of the direction of arrival of maximum disturbance during each month, (*b*) the determination of daily and monthly averages of the number of atmospherics per minute, and (*c*) the correlation of daily and monthly averages of the number of atmospherics per minute with local and distant thunderstorms, mean local temperatures, sunspot numbers and number of magnetically disturbed days. An automatic directional recorder lent by the British Radio Research Board to the Department of Electrical Technology, Indian Institute of Science, Bangalore, in 1924, was available for the investigation and a 24-hour record was obtained on practically every day of the Polar Year. As a cathode ray direction finder was not available, the determination of the "sense" of arrival of the atmospherics and the examination of the intensity of individual atmospherics could not be undertaken.

2. THE DIRECTIONAL RECORDER AND ITS OPERATION.

The recording gear consists of a wooden frame-work supporting a frame aerial which is belt driven by a turret clock and which carries a drum on which the pen of an oscillograph, actuated by the output of an amplifier connected to the aerial, traces the record of the atmospherics. The constructional and other details of the recorder equipment are described in the paper on "The Directional Recording of Atmospherics" by R. A. Watson Watt (*J.I.E.E.*, 1926, **64,** 596) and have therefore been omitted here. A brief description of the circuit is, however, given below.

The winding of the frame aerial is in four sections, two of 20 turns each and two of 10 turns each, of 1·2 mm. diameter bare aluminium wire with a winding pitch of 50 mm. A variable mica condenser of 0·01 microfarads maximum capacity is connected across the winding for tuning the aerial to any desired frequency. The aerial has an inductance of 13·5 mH. and a d.c. resistance of 10·8 ohms with all the four sections in series.

The multi-stage amplifier consists of five resistance-capacity coupled high frequency stages, followed by a detector stage and two transformer-coupled low frequency stages. The triodes used in all the stages except the last are of the Osram D.E.R. type ($R_a = 30{,}000\ \Omega$; $\mu = 8$) and the output stage contains Marconi H.L. 210 type ($R_a = 23{,}000\,\Omega$; $\mu = 20$). The plate batteries are 50 V units of about 2 ampere-hour capacity and the filament batteries are 2 V units each of 120 ampere-hour capacity. A milli-ammeter inserted in the common plate circuit lead to the first seven stages measures the sum of anode currents in these stages and a second milli-ammeter measures the anode current in the output stage. The former milli-ammeter can also be used for measuring the plate voltage by means of a switch and a series resistance. A circuit diagram of the aerial and the amplifier is given in Fig. 1.

The oscillograph inserted in the plate circuit of the output stage consists of a permanent horseshoe magnet with four radial poles each having a coil which carries the output current. The coils are so connected that when a current passes through them, the soft iron armature is deflected from its normal position. A tongue on the armature shaft carries an aluminium girder which holds a siphon pen made of silver tube dipping into an inkwell of adjustable height.

The turret clock drives the frame continuously at a speed of 4 revolutions per hour. This rotation is transmitted to the drum carrying the chart. The drum descends through 3 mm. per revolution. Thus, in the absence of impulses from the amplifier, the oscillograph pen describes a helical trace of 3 mm. pitch on the chart. The arrival of an atmospheric impulse deflects the oscillograph needle and is noted on the chart by a vertical kink transverse to the helical base. The height of this kink can be taken as a measure of the voltage produced across the aerial tuning condenser and its position on the trace gives the time and direction of arrival of the atmospheric. When the paper is taken off the drum and straightened out, the helical trace on the chart resolves itself into 96 approximately horizontal lines each representing one revolution (360° angle) of the drum and fifteen minutes in time at the above speed of rotation.

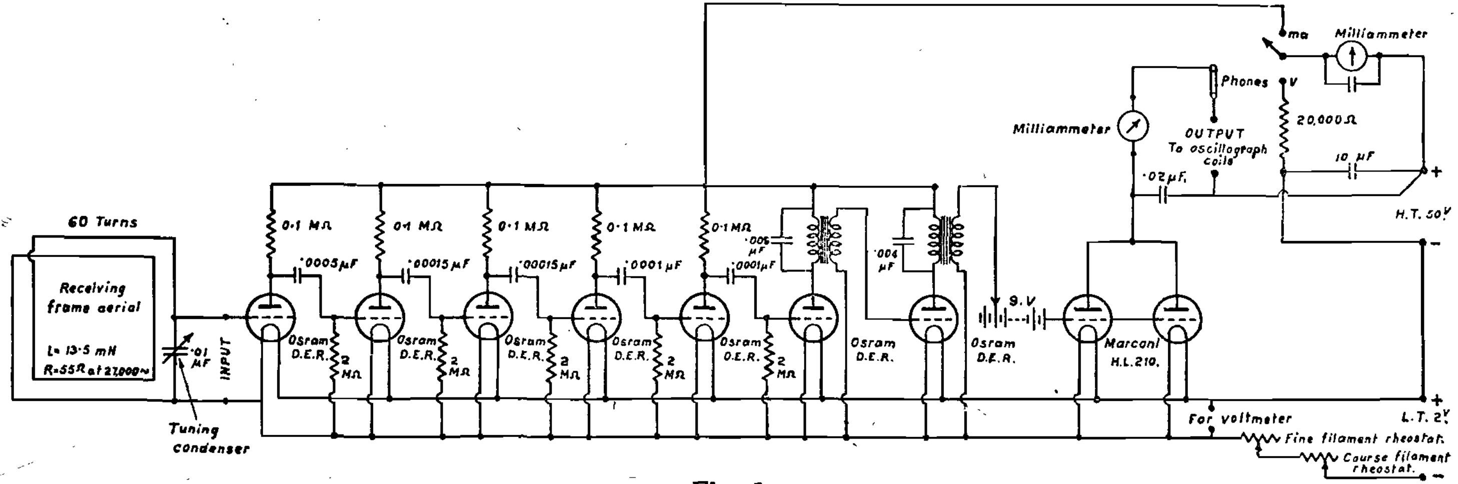


Fig. 1.

Circuit Diagram of the Aerial and the Multistage Amplifier.

3. REDUCTION OF DAILY RECORDS.

Each of the daily records during the month is examined line by line and the most probable direction of arrival of maximum disturbance during each of the 24 hours is marked on the record. The direction which shows the maximum number of kinks of the largest size during the hour is taken as the direction of arrival of the maximum disturbance. Due to the presence of the 180° ambiguity, another direction of arrival of maximum disturbance was always observed, displaced from the first by about 180°. A careful examination of the records further shows that two or more independent directions of disturbance similar to the direction of maximum disturbance may exist only during a quarter or a half-hour.

This multiple distribution was also observed by R. A. Watson Watt and mentioned in his paper on "The Directional Recording of Atmospherics" (*J.I.E.E.*, 1926, **64,** 596).

For determining the hourly direction of arrival of maximum disturbance for the month, the daily records are reduced to the form of a frequency chart, which shows, by means of dots placed underneath the various directions, the number of times the disturbance has arrived from a particular direction at a particular hour during the month. A specimen of the frequency chart is shown in Fig. 2. In the charts there are dense blocks having the largest number of dots

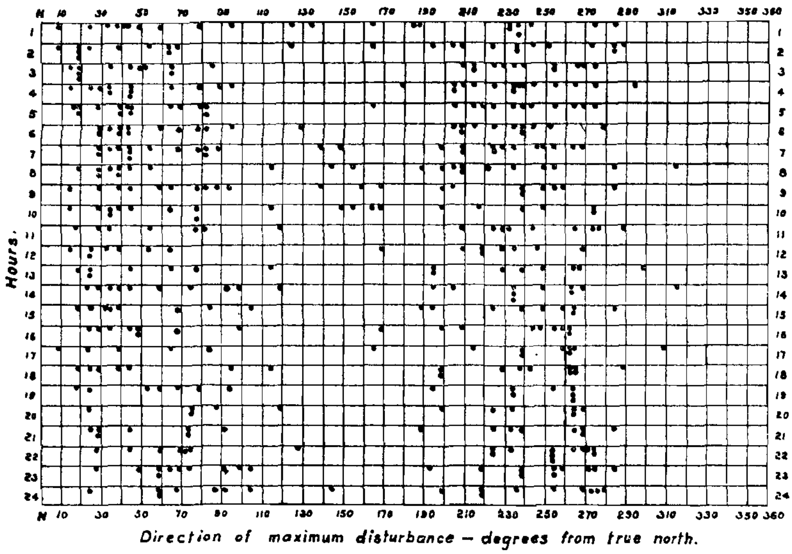
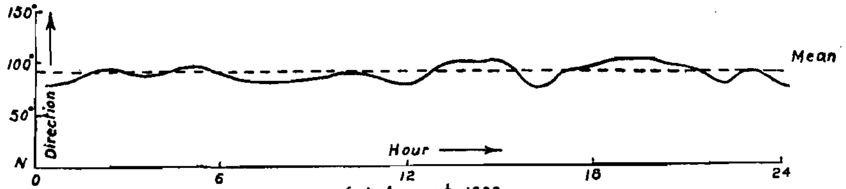
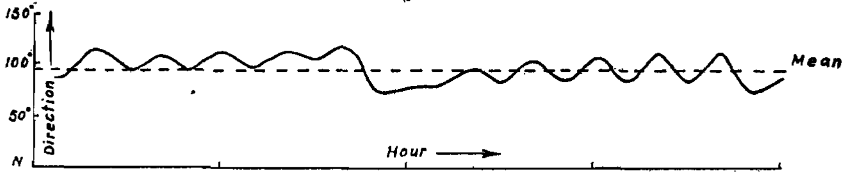


Fig. 2.

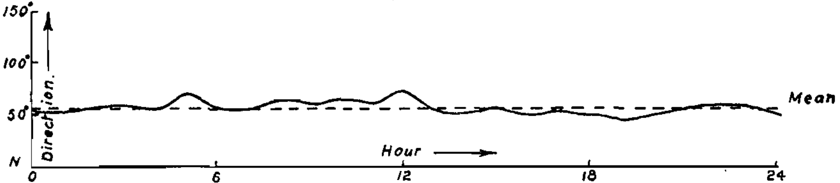
Frequency Chart of Hourly Variation of Direction of Maximum Disturbance.
(February 1933.)



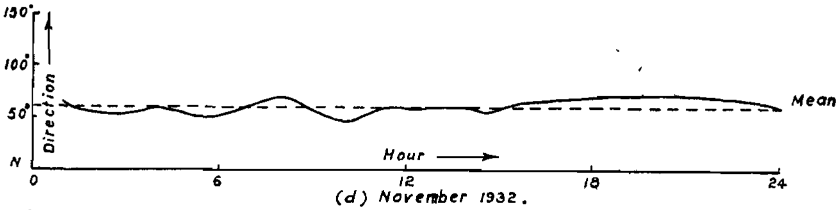
(a) August 1932.



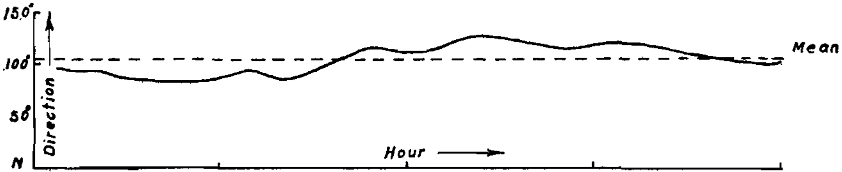
(b) September 1932.



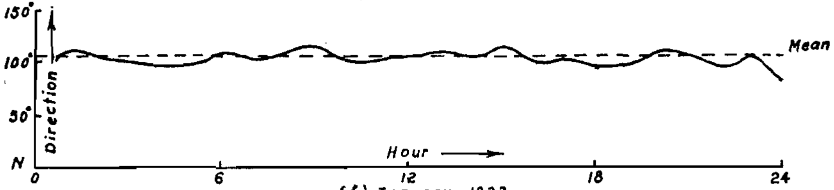
(c) October 1932.



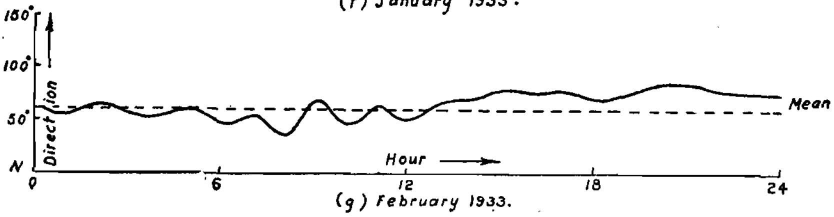
(d) November 1932.



(e) December 1932.

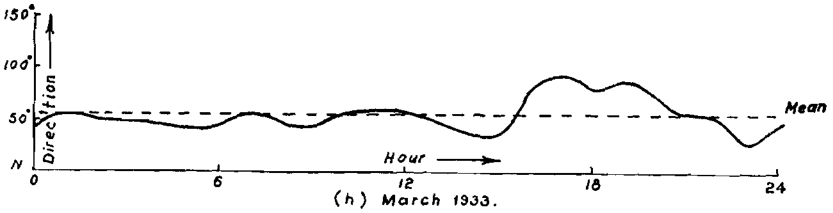


(f) January 1933.

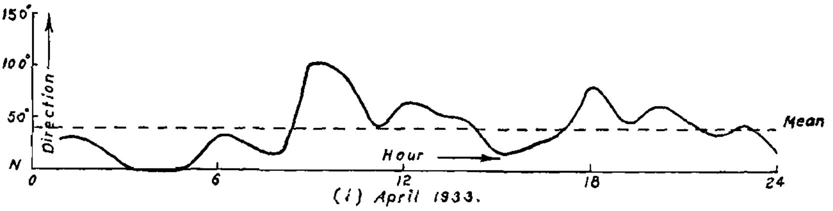


(g) February 1933.

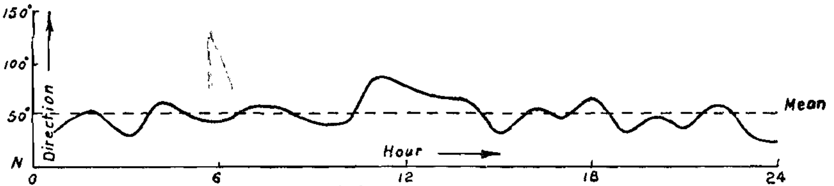
Fig. 3.



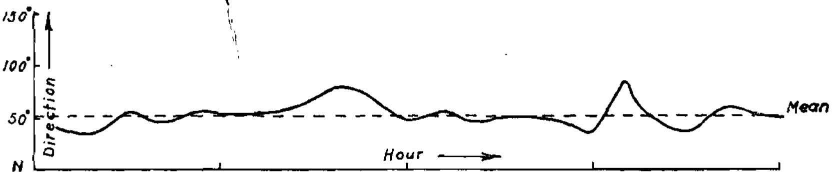
(h) March 1933.



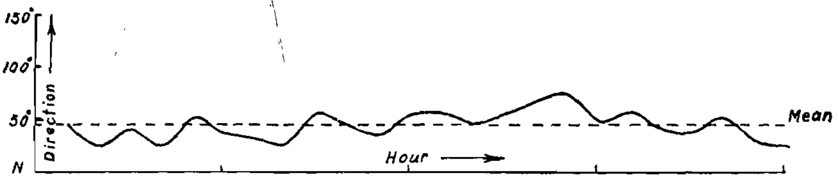
(i) April 1933.



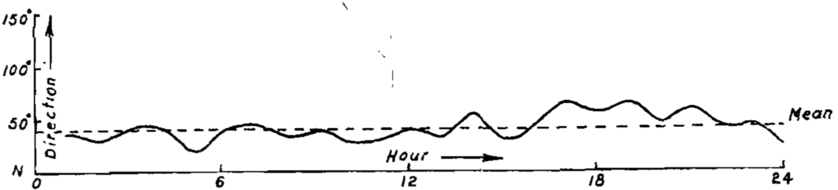
(j) May 1933.



(k) June 1933.



(l) July 1933.



(m) August 1933.

Fig. 3.

Variation of the Hourly Direction of Maximum Disturbance during the Months.

separated by sparse blocks having few or no dots. The "median curve" of these dense blocks, *i.e.*, the direction which has as many dots on one side as on the other is then taken to be the most predominant hourly direction of arrival for the month. The median curve for each month is plotted on a separate sheet for further study as shown in Fig. 3. The median curves appear to vary from hour to hour about mean directions marked in dotted lines in Fig. 3 and plotted against the months as shown in Fig. 4.

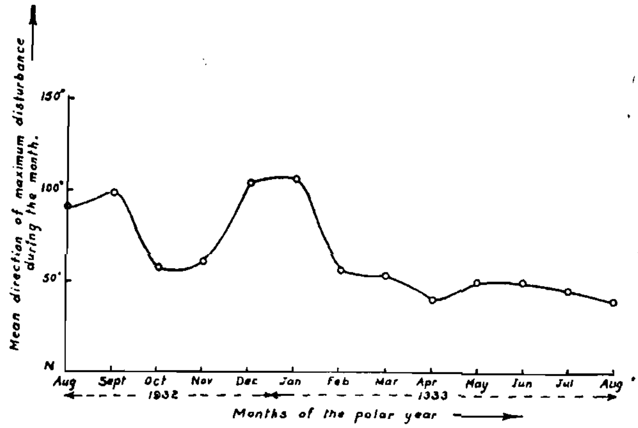


Fig. 4.

Variation of the Monthly Mean Direction of Maximum Disturbance.

The monthly average of the number of atmospherics per minute is arrived at from the daily average of the number of atmospherics per minute which in turn is determined from the hourly number of atmospherics per minute. For determining the hourly number, the number of noticeable kinks in each line of the record (corresponding to fifteen minutes) is counted and divided by fifteen and an average figure for four such lines is then worked out. Fig. 6 shows the daily averages plotted against the days of the month and Fig. 7 shows the monthly averages plotted against the different months. Fig. 8 shows the variation of hourly numbers on a typical summer and a typical winter day during the period under observation.

The change-over from 15 to 27 kc/s. on the 21st November 1932 has resulted in a discontinuity in the graphs for atmospherics shown in Figs. 7, 9, 10 and 11.

4. DEDUCTION OF RESULTS.

Fig. 4 shows that, during the period under observation, the *mean* of the hourly direction of arrival of maximum disturbance for the month varies from 40 to 105 degrees East of true North. Fig. 5 shows the directional limits for the whole year marked (in dotted lines) on a map of South India. It is interesting to observe that the directions of South-West and North-East Monsoons and the directions of the most active thunderstorm areas in Africa and in the East Indies—both of which areas, according to the Australian investigators, Munro and Huxley (Radio Research Board, Australia, *Report* No. 5, 1932) are responsible for the major portion of the atmospherics of the world—fall within the angle marked by the dotted lines.

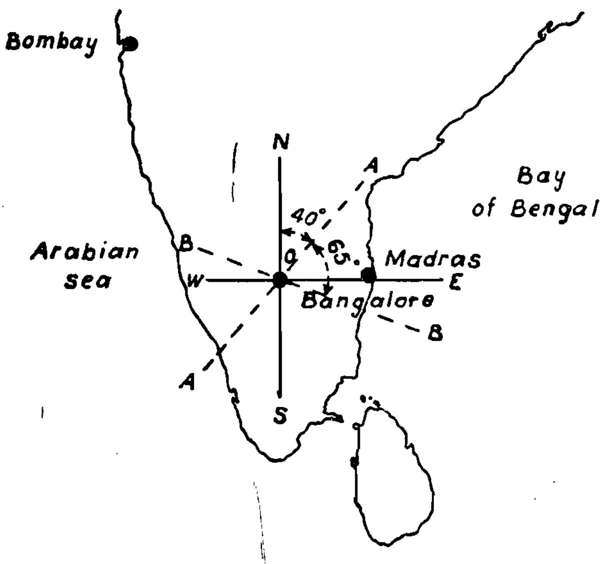
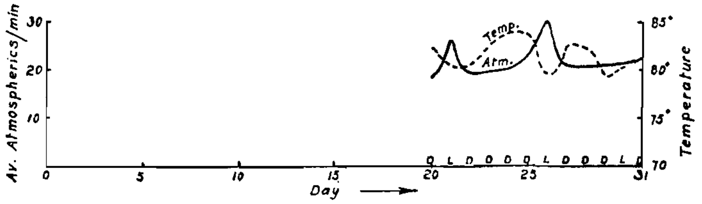


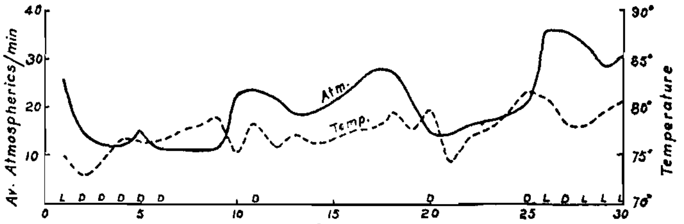
Fig. 5.

Map of South India, showing the Limits within which all Mean Directions of Maximum Disturbance lie.

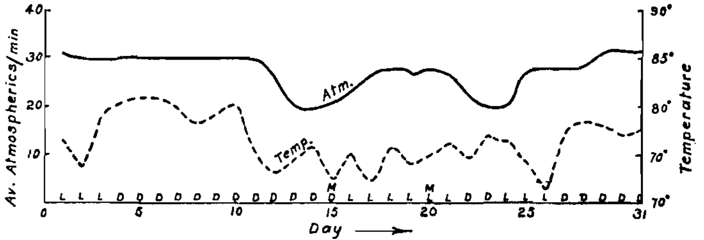
Fig. 3 indicates that during each month the hourly direction of arrival of disturbances varies with the hour of the day about a mean direction. The amplitude of departure is small during the winter months and large during the summer months. Table I shows the maximum and average amplitudes of departure for the various months.



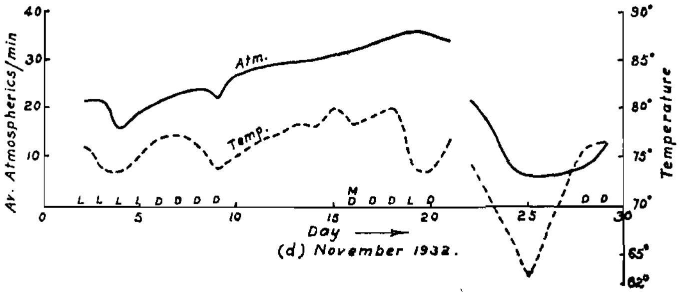
(a) August 1932.



(b) September 1932.

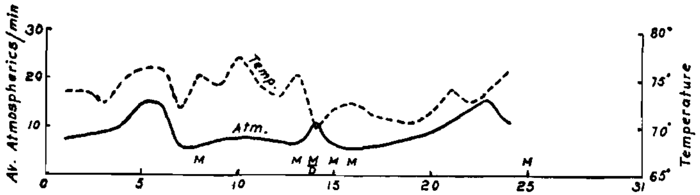


(c) October 1932.

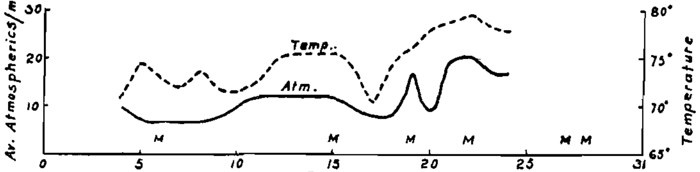


(d) November 1932.

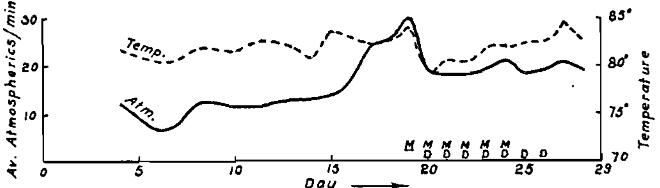
Fig. 6.



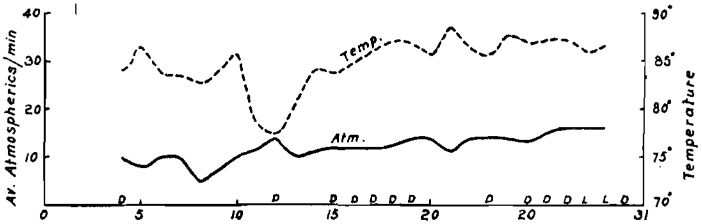
(e) December 1932.



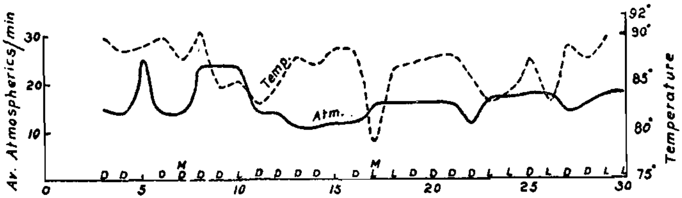
(f) January 1933.



(g) February 1933.

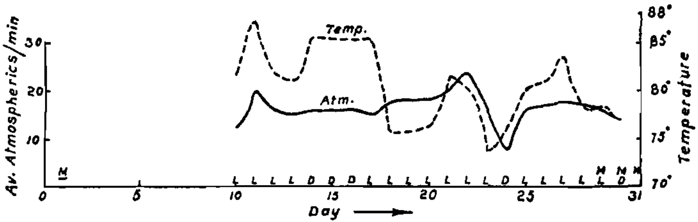


(h) March 1933.

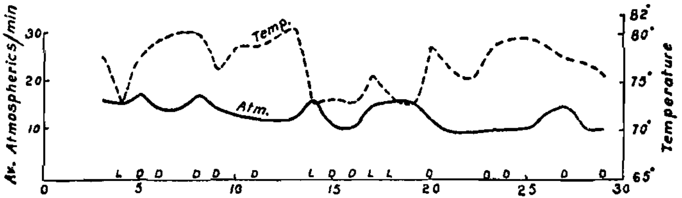


(i) April 1933.

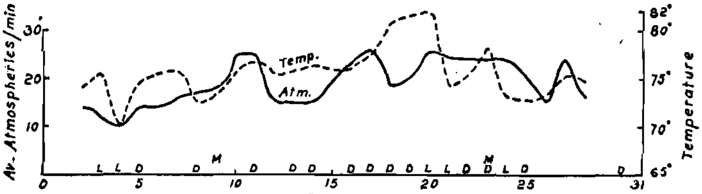
Fig. 6.



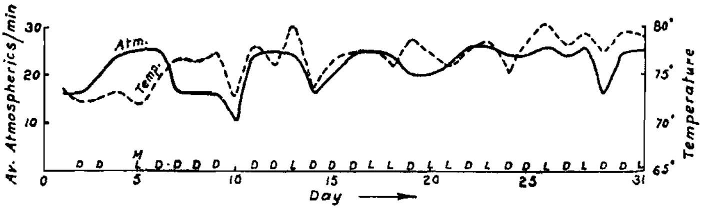
(j) May 1933.



(k) June 1933.



(l) July 1933.



(m) August 1933.

Fig. 6.

Variation of the Daily Average of the Number of Atmospherics per Minute during the Months.

L = Local thunderstorm,
D = Distant thunderstorm,
M = Moderate magnetic disturbance, and
M̲ = Great magnetic disturbance.

TABLE I.

Months		Amplitude of Departure from the Mean	
		Maximum	Average
August 1932	..	14°	8°·75
September ,,	..	20°	13°
October ,,	..	15°	5°·4
November ,,	..	13°	7°·7
December ,,	..	20°	10°
January 1933	..	10°	5°
February ,,	..	30°	10°·8
March ,,	..	40°	17°
April ,,	..	64°	21°·2
May ,,	..	37°	12°
June ,,	..	32°	10°
July ,,	..	28°	11°
August ,,	..	26°	11°·5

It appears therefore that there is a greater constancy as regards the direction of arrival of the maximum disturbance of the atmospherics in winter than in summer. Figs. 6 and 7 show that the average number of atmospherics per minute is higher in summer than in winter months. The monthly averages are given in Table II.

TABLE II.

Months		Monthly Average of the Number of Atmospherics/Min.	
		on 15 kc/s.	on 27 kc/s.
August 1932	..	22	..
September ,,	..	20	..
October ,,	..	27·5	..
November ,,	..	26*	10†
December ,,	..		9
January 1933	..		11
February ,,	..		15
March ,,	..		12
April ,,	..		16
May ,,	..		17
June ,,	..		13
July ,,	..		19
August ,,	..		21

* 20 days' average. † 8 days' average.

Fig. 8 shows that, in general, the hourly number of atmospherics per minute is greater on a summer day than on a winter day. On a winter day, the hourly number of atmospherics per minute is small between the hours 7 and 17 I.S.T. and increases beyond the above limits. On a summer day the hourly number of atmospherics per minute is three to eight times that on a winter day between the same hours (7 and 17 I.S.T.) and increases beyond the above limits.

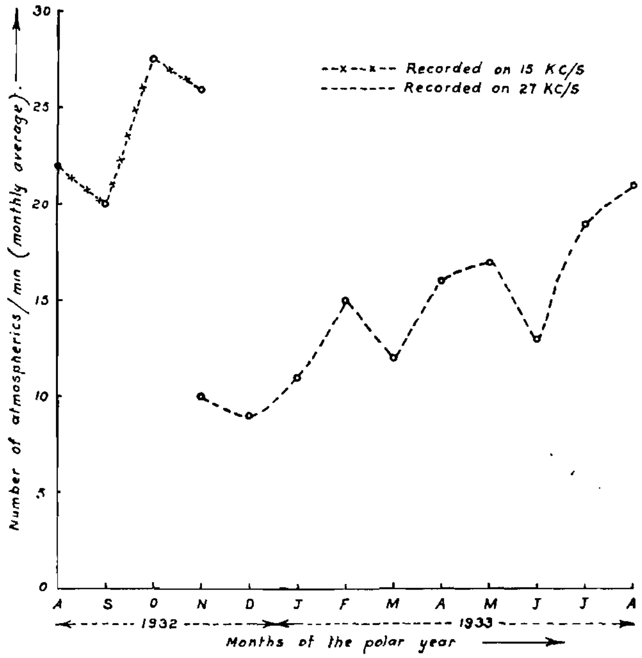


Fig. 7.

Variation of the Monthly Average of the Number of Atmospherics/Min.

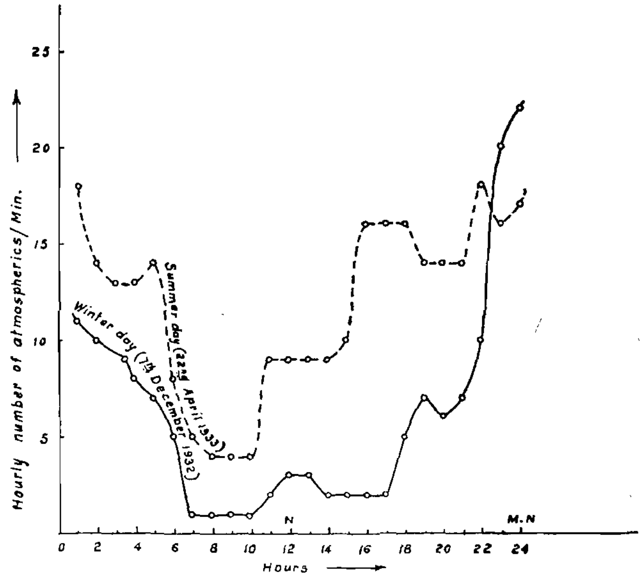


Fig. 8.

Variation of Hourly Number of Atmospherics/Minute during Summer and Winter Days.

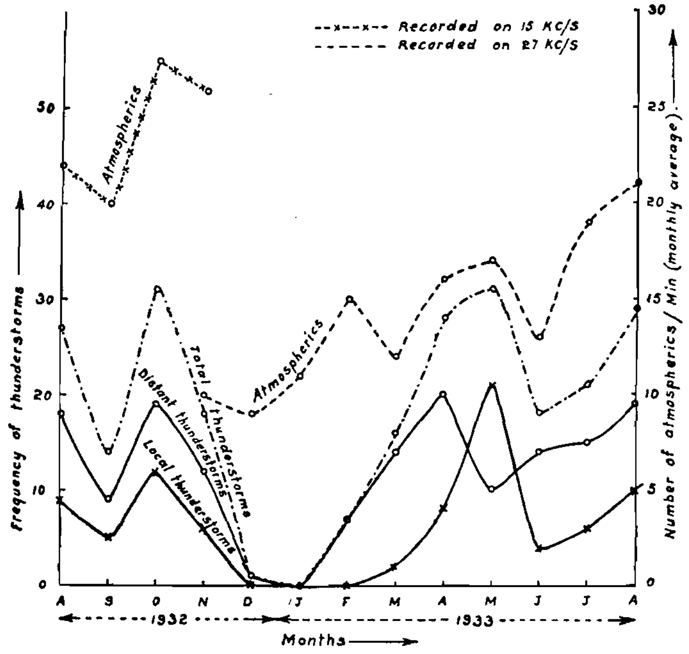


Fig. 9.

Relation between Thunderstorms and Atmospherics.

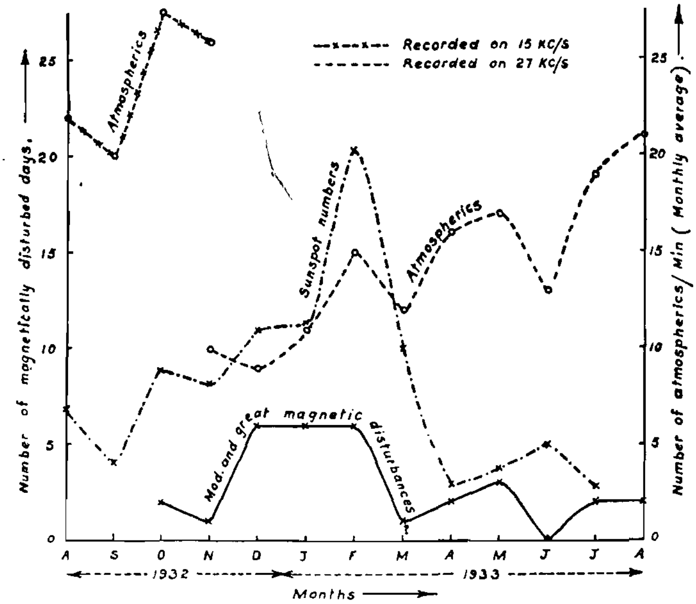


Fig. 10.

Relation between (A) Magnetic Disturbances and Atmospherics, and (B) Sunspot Numbers and Atmospherics.

5. CORRELATION WITH METEOROLOGICAL DATA.

An attempt has also been made to ascertain whether any relationship, direct or inverse, exists between the atmospherics and (*a*) the local and distant thunderstorms, (*b*) the magnetic disturbances, (*c*) the sunspot numbers, and (*d*) the local temperatures in the morning and the afternoon. As so many different factors appear to affect the number of atmospherics, it is not possible to expect an exact correlation between the number of atmospherics and any one of the above factors taken separately. However, Figs. 6, 9 and 10 indicate some correlation in each case. An attempt has been made to correlate the monthly number of atmospherics with the combined effect of local and distant thunderstorms, local temperatures and sunspot numbers during the month and for this purpose "weighted" figures have been used

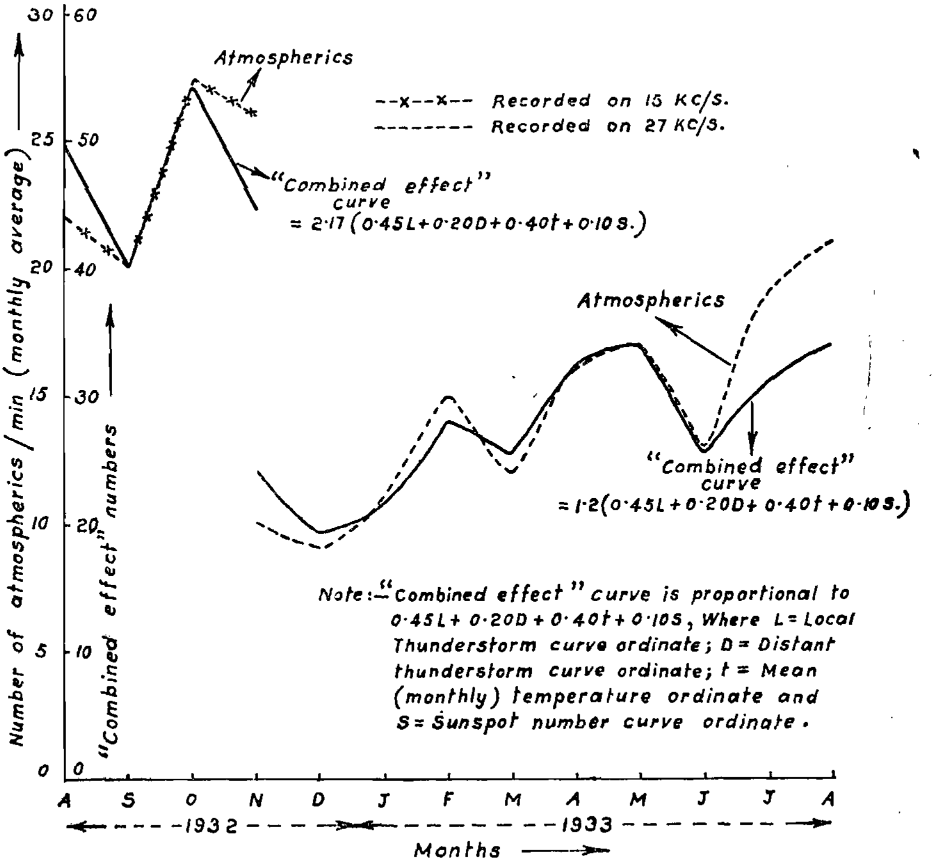


Fig. 11.

Comparison between Atmospherics and Quantity representing the Combined Effect of Local and Distant Thunderstorm Frequencies, Mean Local Temperature and Sunspot Numbers during the Month.

representing the effect of the individual factors. The result is shown in Fig. 11, which shows a similarity between the atmospherics curve and the "combined effect" curve.

(*a*) *Effect on Thunderstorms.*—Since it has been concluded by Watson Watt and other investigators that thunderstorms supply the greater portion of the atmospherics of the world, the correlation of the thunderstorms at Bangalore (*i.e.*, local thunderstorms) and thunderstorms within 120 miles of Bangalore (*i.e.*, distant thunderstorms) with the daily average of the number of atmospherics per minute is of special interest. Fig. 6 shows that on every day on which local thunderstorm occurred the atmospherics reached a high value. The days of local thunderstorms correspond, in general, to peaks in the atmospherics curve.

Fig. 9 further shows that the monthly average of the number of atmospherics per minute bears direct relationship to the frequency of thunderstorms (*i.e.*, total thunderstorms) during the month for the whole of the period under observation except between December 1932 and January 1933 and between February and March 1933.

(*b*) *Effect of magnetic disturbances.*—Fig. 6 shows that on the days of great magnetic disturbances, the atmospherics reach a high value and that on the days of small or moderate disturbance no appreciable increase is observed. Fig. 10 further shows that the monthly average of the number of atmospherics per minute bears a direct relation to the number of days of moderate and great disturbances during the months from February 1933 to August 1933.

(*c*) *Effect of sunspot numbers.*—Fig. 10 indicates that an increase or decrease in the number of sunspots is accompanied by an increase or decrease of atmospheric disturbances respectively between August 1932 and March 1933.

(*d*) *Effect of local temperature.*—Fig. 6 suggests, in general, a direct relationship between the daily number of atmospherics per minute and the mean of the local temperatures at 1020 and 1700 I.S.T. A careful examination of the atmospherics and the temperature curves further shows that the atmospherics curve varies directly as the temperature curve or the curve shifted forward by a day.

During some months, the atmospherics curve varies directly as the temperature curve for a portion of the month and then varies directly as the temperature curve shifted forward by a day for the rest of the month.

It appears therefore that the atmospherics on a particular day may be related either to the mean temperature of the same day or to the mean temperature of the previous day.

It may be stated that Austin's experiments carried out near Washington during 1924-26 indicated a direct relationship between the atmospherics and (*a*) distant thunderstorms within 200 miles of Washington, and (*b*) local temperatures averaged in 10-day periods. The direct relationship of the atmospherics with the local thunderstorms, mean local temperature of the same or previous day, sunspot numbers and moderate and great magnetic disturbances as shown by present experiments are, however, new results.

6. CONCLUSION.

The following conclusions have been arrived at by the authors:—

(1) The mean of the hourly direction of arrival of maximum disturbance at Bangalore for the period August 1932 to August 1933 varies from 40° to 105° East of true North and there is a greater constancy of the hourly direction of arrival of the maximum disturbance in winter than in summer months.

(2) The average number of atmospherics per minute is higher in summer than in winter. The hourly average number of atmospherics per minute is several times higher on a summer day than on a winter day.

(3) On each day that a thunderstorm occurs at Bangalore, the daily number of atmospherics per minute reaches a high value. In the month in which the frequency of occurrence of thunderstorms is high the monthly average of the number of atmospherics per minute is also high.

(4) A day of "great" magnetic disturbance is associated with a high daily number of atmospherics per minute. An increase or decrease of sunspots appears to be accompanied by an increase or decrease of atmospheric disturbances respectively during eight months of the period under observation.

(5) The atmospherics on a particular day appear to be related to the mean local temperature of the same day or to the mean local temperature of the previous day.

7. ACKNOWLEDGMENTS.

The authors desire to thank Mr. M. L. Venkataramiah for assisting them in setting up the atmospherics recorder and Professor F. N. Mowdawalla and Mr. K. Sreenivasan for taking very keen interest in their work and discussing the results of the experiments. They also desire to thank the Indian Meteorological Department and Mr. Seshachar, Meteorologist to the Government of Mysore, for kindly supplying them with the various meteorological data for their use.

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STUDIES IN DIELECTRICS.

PART I. THE EFFECT OF SUPERIMPOSED MAGNETIC FIELDS ON THE BREAKDOWN VOLTAGE OF DIELECTRICS.

By N. V. Narayanaswami and F. N. Mowdawalla.

The problem of the effect of superimposed magnetic fields on the dielectric properties of insulating materials has hitherto received very little attention. Considerable work has been done by physicists on the effect of magnetic fields on electrical discharges in gases, and indicates that a magnetic field exercises considerable influence on the sparking potential of, as well as the discharge current in, gases. The effect of unidirectional magnetic fields on the dielectric constant of some gases has also been investigated and found to be negligible. Recently some interesting observations relating to the effect of magnetic fields on breakdown voltage and power loss have been made. Monkhouse (*Proc. Phys. Soc.*, 1928-29, **41**, 83) observed that the spark-over voltage of air was altered when it was subjected to a magnetic field, the magnitude and sign of the change depending on the direction and nature (whether unidirectional or alternating) of the field and the shape of the electrodes. R. Schmid (*Ann. der Physik*, 1932, **14**, 809) has studied the impulse breakdown of air and observed that a unidirectional longitudinal magnetic field of 14 000 gauss lowered the puncture voltage by as much as 25 per cent. while a transverse field increased it by about the same amount. His results show that the magnitude of the change is greatest with an impulse voltage, smaller with a 500-cycle A-C voltage and negligible with a D-C voltage. According to these investigators, the nature of the electrodes and the length of the spark gap greatly influence the change produced by the magnetic field.

A study of the literature on the subject indicates that the influence of magnetic fields on the dielectric properties of solid and liquid insulating materials used by engineers is just beginning to be investigated and sufficient data are not yet available. A. Smurrow (*Archiv. f. Elektrot*, 1929, **22,** 31) has concluded from theoretical considerations that a magnetic field should affect the dielectric properties of insulating materials, and has experimentally observed a reduction in the B. D. V. of transformer oil and air with both longitudinal and transverse alternating magnetic fields. A number of anomalous phenomena relating to insulation failures and corona discharges which were observed in connection with the operation of high voltage networks led Monkhouse (*loc. cit.*) to investigate the effect of magnetic fields on the B. D. V. of some solids and liquids with a view to determine if the abnormal behaviour could be explained thereby. Working with magnetic fields of intensities up to about 6 500 gauss, he observed that an alternating field, whether longitudinal or transverse, increased the B. D. V. of insulating oil by about 9 per cent. while an unidirectional field decreased it by the same amount. The B. D. V. of pressboard was decreased to the extent of 25 per cent. by a magnetic field, whether alternating or unidirectional, when it was longitudinal or parallel to the electric field. On the other hand, no effect was observed when it was transverse or at right angles to the electric field. A. Smurrow (*E.T.Z.*, 1930, **51**, 1459) has observed that the B. D. V. of mica was increased by as much as 50 per cent. with a transverse field while no effect was observed with a longitudinal field. These results indicate that, in some cases, even low magnetic fields have considerable influence on the B. D. V. of insulating materials. As such a change in the dielectric strength of insulating materials would affect the design of insulation of electrical machinery and apparatus and as the observations of Monkhouse and Smurrow were not supported by the work of other investigators, it was decided to carry on further investigation of the matter using stronger magnetic fields and a wider range of materials. The materials tested were Air, Transformer and Switch oils and some solid dielectrics, *e.g.*, Manilla paper, Presspahn, Pressboard, Kraft paper and Glass. Detailed specifications relating to these materials are given in the Appendix.

EXPERIMENTAL.

Electromagnet.—For the production of magnetic fields of high intensity, the electromagnet shown in Fig. 1 was used. The core was formed of stalloy stampings but tapered solid pole pieces, as shown in the figure, were used for unidirectional fields used in the present experiments. The air-gap between the poles was adjustable and depended upon the position in which the pole-pieces were clamped. The normal current carrying capacity of the coils was 12 amperes but for short periods the current could be pushed up to 20 amperes with artificial ventilation by means of an electric fan. A curve connecting field strength with gap length is shown in Fig. 2, which shows that with 20 amperes excitation and 5 mm. air-gap, a gap flux density of 18 000 gauss could be obtained. This was the maximum value of the flux density used in the experiments.

Test Electrodes.—The electrodes used in the experiments are shown in Figs. 3 to 6. Fig. 3 shows the arrangement adopted for the measurement of the B. D. V. of air and oil with longitudinal magnetic fields. The electrodes consisted of two 1″ diameter copper discs about $\frac{1}{64}$″ thick, which were pasted to two $3'' \times 2'' \times \frac{1}{32}''$ glass plates by a mixture of rosin and beeswax. This rosin compound showed no tendency to dissolve in oil. An ebonite piece cut as shown in the diagram and having

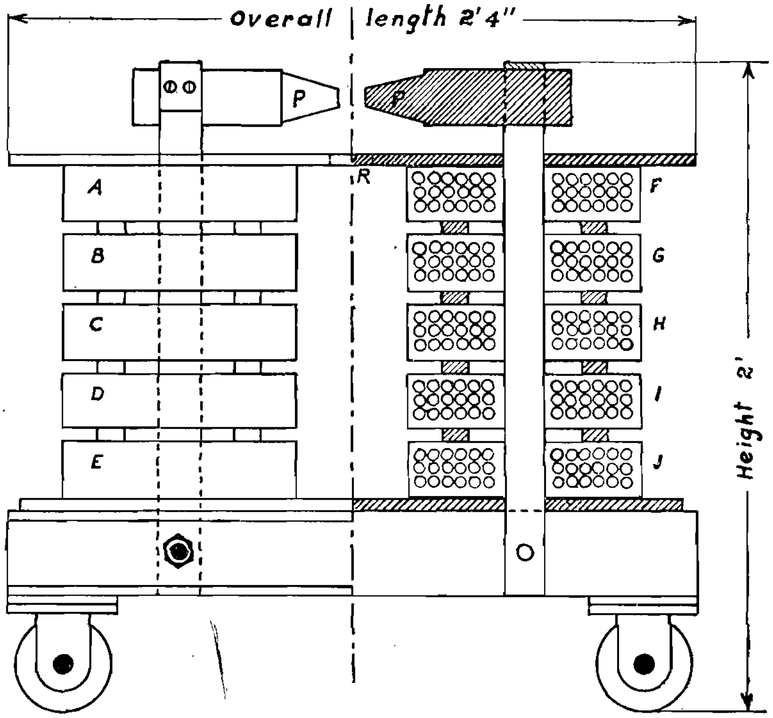

Fig. 1.

General Appearance of Electromagnet.

PP—Solid Poles.

A, B, C, D, E, F, G, H, I & J—Coils 600 turns each of No. 11 D.C.C. Copper wire.

R—Receptacle in insulating board for test cell.

the same external dimensions as the glass plates was used as spacer between them and was fixed to them with the same rosin compound so as to form a rectangular cell with glass sides and ebonite edges. The electrical connection from one of the electrodes was taken to the top by means of a thin copper wire soldered to it; from the other, the connection was taken to the bottom by means of a similar copper wire passing through the ebonite base of the cell. The wire at the top was connected to the high voltage terminal of the transformer and that at the bottom to earth. When the cell was introduced between the poles of the magnet the electric field was longitudinal or parallel to the magnetic field. The over-all thickness of the cell used for the B. D. V. of air was 9 mm. and a flux density of 12 500 gauss in the dielectric was obtainable with an exciting current of 20 amperes. The cell used for the B. D. V. of oil had an over-all thickness of 7 mm. and a field strength of 14 000 gauss was obtainable. For tests with oil the cell was carefully cleaned prior to each experiment so as to exclude dirt, fibres and other impurities, and a small ebonite cover was provided.

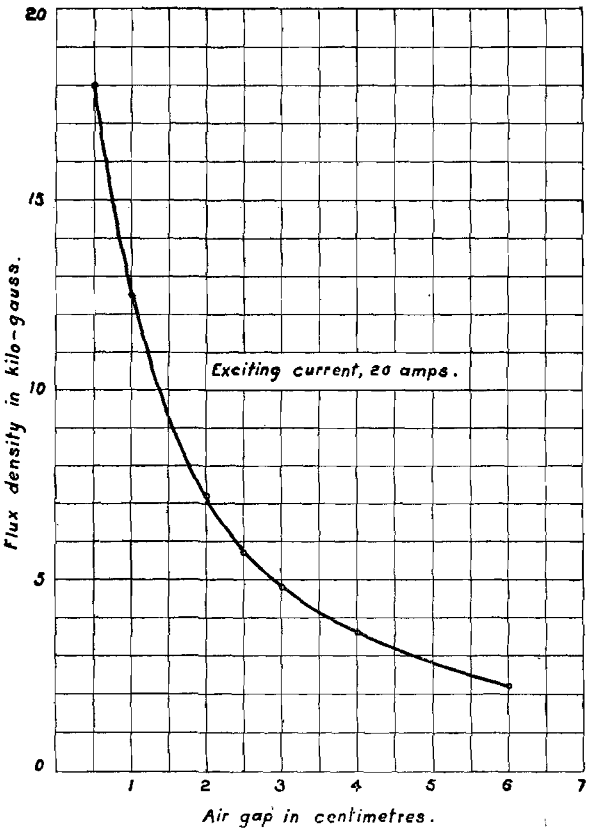

Fig. 2.

Air Gap Flux Density for Different Gaps in Electromagnet.

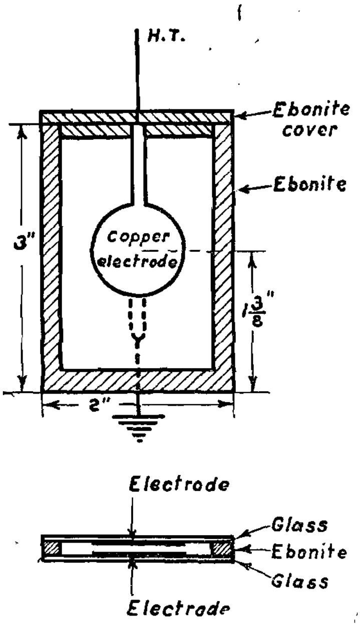

Fig. 3.

Electrodes for B. D. V. Measurements on Air and Oil with Longitudinal Magnetic Fields.

The measurement of the B. D. V. of air and oil with transverse magnetic fields was carried out with a similar cell with glass sides and ebonite edges as shown in Fig. 4. In this case, however, the electrodes were $\frac{1}{8}''$ diameter brass spheres turned at one end of two brass rods about 2″ long. The rods were threaded at the other end for screwing into threaded holes in the ebonite sides of the cell. Lock nuts were provided for preventing the movement of the rods after the gap had been adjusted. When the cell was introduced between the magnet poles the electric field was transverse or perpendicular to the magnetic field. The cell had an over-all thickness of 1 cm. and when inserted in an air gap of 1·1 cm. a field intensity of 11 500 gauss was obtained.

The electrodes used for the measurement of the B. D. V. of solids with longitudinal magnetic fields are shown in Fig. 5 and consisted of 1″ diameter brass discs cut out of $\frac{1}{64}''$ brass sheet and pasted on $4'' \times 3\frac{1}{2}''$ mica plates 1 mm. thick. The test sample cut to 2″ square was held

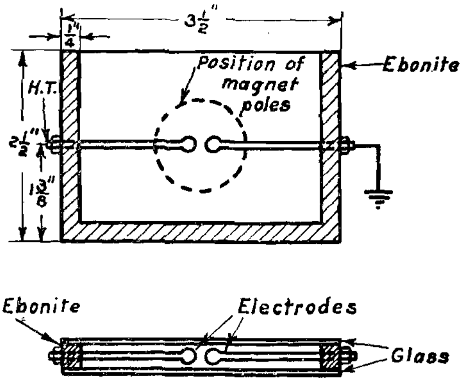

Fig. 4.

Electrodes for B. D. V. Measurements on Air and Oil with Transverse Magnetic Fields.

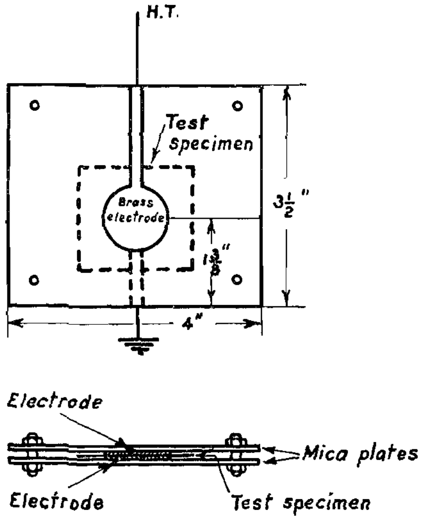

Fig. 5.

Electrodes for B. D. V. Measurements on Solids with Longitudinal Magnetic Fields.

between the electrodes by means of brass screws at the corners of the mica plates. The over-all thickness of the cell did not exceed 4 mm. so that it could be introduced in a 5 mm. air gap and a field intensity of 18 000 gauss obtained. This cell was found to be suitable for the measurement of the B. D. V. of all materials except glass. For glass of which the samples were 1·2″ square, the diameter of the electrodes had to be reduced from 1″ to $\frac{1}{8}''$ in order to provide sufficient flash-over distance between them over the surface of the test specimen.

Fig. 6 represents the arrangement used for the B. D. V. of the insulating papers with transverse magnetic fields. The electrodes had necessarily to be of small diameter in order that they could be introduced in a small air gap, and consequently $\frac{1}{16}''$ diameter brass pins were used. These were passed through two ebonite pieces cut into the shape shown in the figure. The test samples cut into small rectangular pieces 2·5 cms. x 4 mm. were held in position between the electrodes by means of screws at the top and bottom of the ebonite pieces. In some cases, wider specimens were required as they had to be folded over on the sides of the ebonite in order to prevent flash-over from the high tension electrode to the magnet poles.

High Tension Supply.—All the B. D. V. measurements were conducted with 25-cycle alternating current. The general scheme of connections is shown in Fig. 7. The testing transformer was rated at

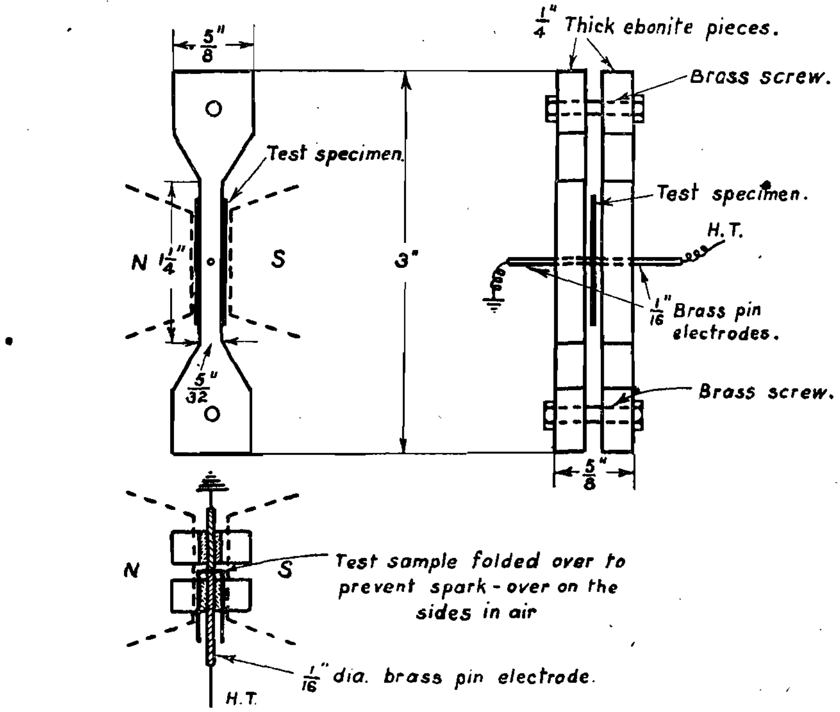

Fig. 6.

Electrodes for B. D. V. Measurements on Solids with Transverse Magnetic Fields.

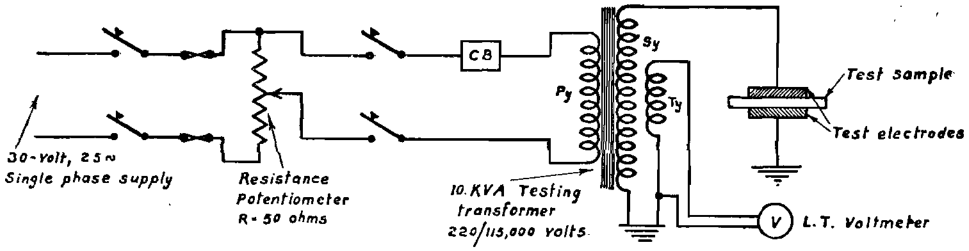

Fig. 7.

General Scheme of Connections.

10 kVA, 220/115 000 volts, and provided with a tertiary winding for voltage measurement.

Method of Testing.—In order to obtain satisfactory results it was necessary to prepare the samples very carefully before the tests. The oil was thoroughly dried by heating and passing through a filter press two or three times, after which it was stored in glass-stoppered bottles. The samples of insulating paper were dried in a closed oven. In the case of air, the temperature, pressure and humidity were not under control but it was assumed that they remained constant during each set of tests which lasted for about an hour. With the test cell in position, the B. D. V. of air was measured alternately with and without the magnetic field. The test voltage in each case was rapidly raised (about 1 kV per second) from zero to the disruptive value consistently with its value being read accurately on the voltmeter. The mean of a large number of readings was taken as the true B. D. V. of air. This method was also adopted in the case of all the other dielectrics.

In the case of oil, each shot produced a small amount of carbon and also removed a small amount of moisture. After each shot, the oil was stirred with a clean glass rod in order to distribute the carbon particles. As the tests with and without the magnetic field alternated, the very small changes in the oil produced at each shot may be regarded as affecting both sets of readings equally.

With solids, the specimen had to be renewed after each test and therefore a large number of test samples was required. A certain amount of error was therefore introduced due to the non-uniformity of the material but, as the average of a large number of readings was taken as the true B. D. V. and as the measured thickness of the various samples was found to be remarkably uniform, this error may be regarded as being negligible.

RESULTS.

Air.—The readings for the B. D. V. of air under two different sets of conditions are given in Tables I and II, the values representing the average of the number of readings in each set. The ratio of B. D. V. with magnetic field to that without the field is also given.

TABLE I.

Air.—			
	Barometric Pressure	.. ..	68·6 cms.
	Temperature	.. ..	24·5°C.
	Relative Humidity	.. ..	70·2 per cent

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*
Gauss			kV	kV	
10 500	Longitudinal	50	6·25	6·25	1·00
12 500	,,	,,	6.00	6.00	1·00

---

* Ratio refers to the ratio of the B. D. V. with magnetic field to that without the field.

TABLE II.

Air.—Barometric Pressure .. .. 68·65 cms.
Temperature .. .. 24·5°C.
Relative Humidity .. .. 66·7 per cent.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*
Gauss			kV	kV	
10 000	Transverse	50	7·90	7·90	1·00
11 500	,,	,,	6·95	6·90	1·01

* Ratio refers to the ratio of the B. D. V. with magnetic field to that without the field.

In all cases this ratio is unity, indicating that the magnetic field has no effect on the 25 cycle B. D. V. of air. This result is not in agreement with that of Monkhouse (*loc. cit.*) and Smurrow (*loc. cit.*) but seems to agree with that of R. Schmid (*loc. cit*). As the main object of the investigation was to study liquid and solid dielectrics further work on air at different pressures and temperatures was not continued.

The variation of successive breakdown readings is shown in Fig. 8. The maximum variation from the mean value is not more than 4 per cent.

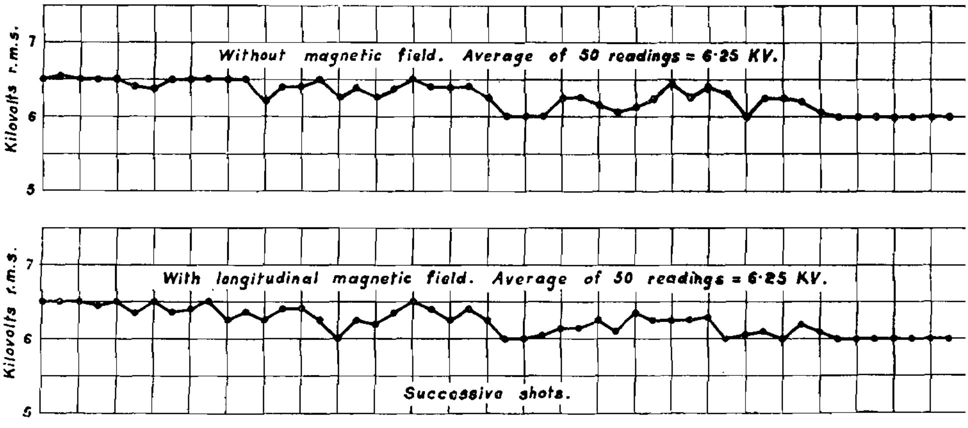

Fig. 8.

Variation of B. D. V. of Air with Successive Shots.

Oils.—The results for transformer and switch oils are given in Tables III and IV.

TABLE III.

Transformer Oil.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
14 000	Longitudinal	60	15·70	15·80	0·99	0·99
,,	,,	100	16·70	17·00	0·98	
,,	,,	100	18·00	18·10	0·99	
11 500	Transverse	60	8·95	8·65	1·03	1·02
,,	,,	100	6·00	5·95	1·01	
,,	,,	100	8·30	8·10	1·02	

TABLE IV.

Switch Oil.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*
Gauss			kV	kV	
14 000	Longitudinal	100	14·80	14·80	1·00
11 500	Transverse	100	7·80	8·00	0·98

* Ratio refers to the ratio of the B.D.V. with magnetic field to that without the field.

The ratio of the B. D. V. with and without the magnetic field is given for the several cases and differs but little from unity in all cases. It is therefore concluded that the magnetic field has an inappreciable, if any, effect on the B. D. V. of mineral oils. R. Schmid's (*loc. cit.*) conclusion that a unidirectional magnetic field has no effect on the dielectric current in certain liquid dielectrics appears to confirm this result. On the other hand, Monkhouse and Smurrow (*loc. cit.*) have reported appreciable changes in the B. D. V. of transformer oil with lower magnetic fields.

Individual readings shown in Fig. 9 indicate an initial rise in the B. D. V. of the sample due probably to the effect of successive shots.

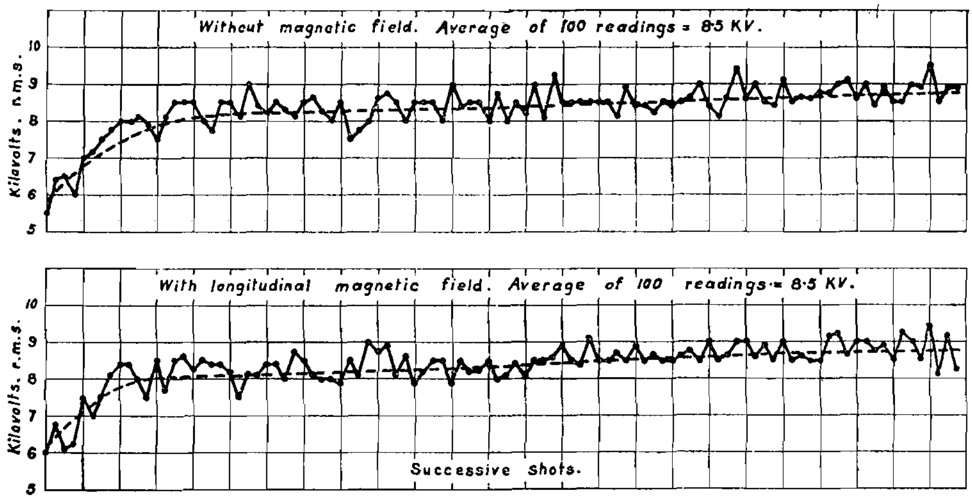

Fig. 9.

Variation of B. D. V. of Transformer Oil with Successive Shots.

As this affects both the sets of readings equally no error is introduced thereby. The dotted curve shows the mean value of the B. D. V. at each point and the maximum variation therefrom is small.

Solids :—Results relating to solids are given in Tables V to IX.

TABLE V.

Manilla Paper.—No. of layers, 2 ; thickness of each layer, 5 mils.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
18 000	Longitudinal	30	1.75	1·75	1·00	0·98
,,	,,	30	1.53	1·58	0·97	
,,	,,	30	1·55	1·63	0·95	
,,	,,	30	1.70	1·70	1·00	
,,	Transverse	30	1.95	1·93	1·01	1·01
,,	,,	30	1·93	1·93	1·00	
,,	,,	30	1·83	1·80	1·01	
,,	,,	30	1·80	1·78	1·01	

* Ratio refers to the ratio of the B.D.V. with magnetic field to that without the field.

TABLE VI.

Presspahn.—No. of layers, 1 ; thickness of each layer, 10 mils.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
18 000	Longitudinal	30	1·75	1·85	0·95	0·96
,,	,,	25	1·68	1·75	0·96	
,,	,,	15	1·98	2·00	0·99	
,,	,,	25	1·83	1·90	0·96	
,,	Transverse	20	2·20	2·00	1·10	1·06
,,	,,	20	2·40	2·25	1·07	
,,	,,	20	2·38	2·30	1·03	
,,	,,	20	2·30	2·20	1·05	
,,	,,	20	2·10	2·00	1·05	

*Ratio refers to the ratio of the B.D.V. with magnetic field to that without the field.

TABLE VII.

Pressboard.—No. of layers, 1 ; thickness of each layer, 5 mils.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
18 000	Longitudinal	25	2·23	2·33	0·96	0·96
,,	,,	25	2·08	2·20	0·94	
,,	,,	25	2·10	2·13	0·99	
,,	,,	25	2·08	2·18	0·95	
,,	,,	25	2·13	2·20	0·97	
,,	,,	25	2·30	2·38	0·97	
,,	Transverse	25	3·50	3·40	1·03	1·04
,,	,,	25	3·55	3·45	1·03	
,,	,,	25	3·35	3·20	1·05	
,,	,,	25	3·25	3·15	1·03	
,,	,,	25	3·33	3·23	1·03	
,,	,,	25	3·40	3·28	1·04	

* Ratio refers to the ratio of the B.D.V. with magnetic field to that without the field.

TABLE VIII.

Kraft Paper.—No. of layers, 1 ; thickness of each layer, 10 mils.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
18 000	Longitudinal	25	2·23	2·18	1·02	1·02
,,	,,	25	2·18	2·13	1·02	
,,	,,	25	2·40	2·38	1·01	
,,	,,	25	2·38	2·35	1·01	
,,	,,	25	2·45	2·40	1·02	
,,	,,	25	2·40	2·30	1·04	
,,	Transverse	25	3·13	3·00	1·04	1·04
,,	,,	25	3·10	3·00	1·03	
,,	,,	25	3·05	2·90	1·05	
,,	,,	25	3·00	2·90	1·04	
,,	,,	25	3·00	2·88	1·04	
,,	,,	25	3·00	2·88	1·04	

*Ratio refers to the ratio of the B. D. V. with magnetic field to that without the field.

TABLE IX.

Glass.—No. of layers, 1 ; thickness of each layer, 4 mils.

Magnetic Field Strength	Mutual direction of electric and magnetic fields	No. of B. D. V. readings taken in each set	B. D. V. with magnetic field	B. D. V. without magnetic field	Ratio*	Average Ratio
Gauss			kV	kV		
18 000	Longitudinal	25	7·25	7·00	1·04	1·03
,,	,,	25	7·25	7·15	1·02	
,,	,,	25	7·25	7·05	1·03	
,,	,,	25	7·40	7·20	1·03	

*Ratio refers to the ratio of the B.D.V. with magnetic field to that without the field.

There seems to be a small but definite effect of the magnetic field in all cases. Longitudinal fields seem to lower the B. D. V. of manilla paper, presspahn and pressboard but to increase that of kraft paper and glass. The effect of transverse fields seems to be to increase the B. D. V. in all cases, the maximum increase being about 6 per cent. in the case of presspahn. These results do not agree with those of Monkhouse (*loc. cit.*) who reports a considerably greater effect with smaller magnetic fields. It would appear from these results that the influence of even very intense magnetic fields is not so great as to affect the insulation of machinery and apparatus and it therefore does not seem to be necessary to take this factor into consideration in the design of insulation for electrical machinery and apparatus.

Fig. 10 represents the variation of B. D. V. of a number of test samples of pressboard and indicates larger variations than in air and oil. Similar variations were also noticed in the case of the other materials.

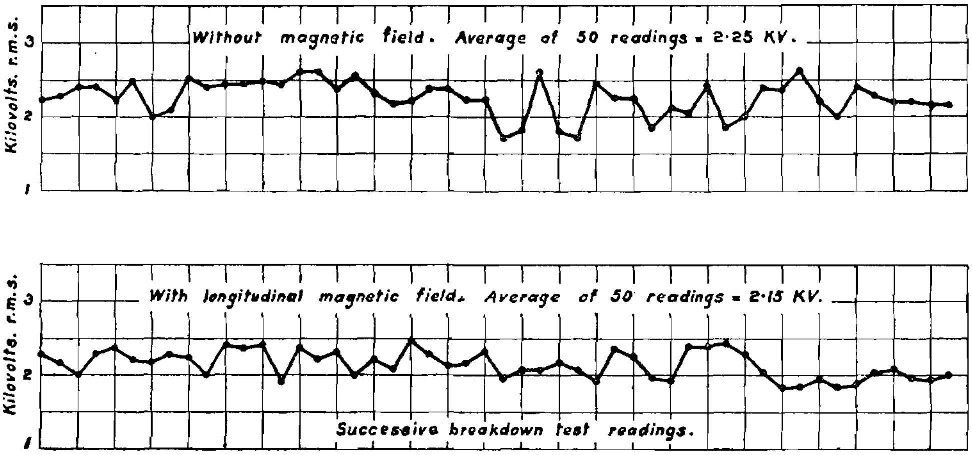

Fig. 10.

Variation of B. D. V. of Pressboard in Successive Tests.

SUMMARY.

The effect of superimposed unidirectional magnetic fields on the 25-cycle breakdown voltage of air, liquid and solid dielectrics has been studied and the following conclusions drawn :—

(1) Longitudinal magnetic fields up to 12 500 gauss and transverse fields up to 11 500 gauss do not affect the B. D. V. of air at the laboratory temperature and pressure.

(2) The effect of longitudinal magnetic fields up to 14 000 gauss and transverse fields up to 11 500 gauss on the B. D. V. of mineral oils is negligible.

(3) Magnetic fields up to 18 000 gauss, whether transverse or longitudinal, have an inappreciable effect on the B. D. V. of manilla paper.

(4) A longitudinal magnetic field of 18 000 gauss decreases the B. D. V. of presspahn by about 4 per cent.; a transverse field of the same strength increases it by about 6 per cent.

(5) A longitudinal magnetic field of 18 000 gauss decreases the B. D. V. of pressboard by about 4 per cent.; a transverse field of the same strength increases it by about the same amount.

(6) A longitudinal magnetic field of 18 000 gauss increases the B. D. V. of kraft paper by about 2 per cent. and a transverse field of the same strength increases it by about 4 per cent.

(7) The increase in the B. D. V. of glass by a longitudinal magnetic field of 18 000 gauss is about 3 per cent.

(8) All these changes are much smaller than those reported by Monkhouse and Smurrow working with weaker magnetic fields.

In conclusion, we wish to express our thanks to Mr. B. Nanjundiah, B.Sc., for considerable assistance in the construction of the electromagnet and in the preliminary experiments.

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APPENDIX.

Specifications of Materials.

Transformer Oil: Transil No. 10–C.

Specific gravity		0·900
Flash point	not lower than	270°F.
Fire point	,,	300°F.
Redwood Viscosity at 75°F.		62–65″
Alkalies, sulphur, etc.		None.

Switch Oil: Transil No. 6.

Specific gravity		0·885
Flash point	not lower than	360°F.
Fire point	,,	400°F.
Redwood Viscosity at 75°F.		100–105″
Alkalies, sulphur, etc.		None.

Manilla paper.—This material is a tough, pliable paper made from manilla rope stock and is used for wrapping on wires and cables and in the manufacture of pad and layer insulation for transformers and also in the manufacture of treated paper tape.

Colour: dull brown; Thickness, 5 mils.

Presspahn.—This is a tough, smooth, flexible fibre material with a high mechanical strength, and is very moisture resistant. The surface is calendered. It is used in the manufacture of slot tubes and as inter-coil insulation in transformers.

Colour: yellowish brown; Thickness, 10 mils.

Pressboard.—This is a paper composed of 50 per cent. cotton fibre and 50 per cent. jute and the material is given a varnish treatment to improve its moisture-resisting properties. It is used extensively in the insulation of oil-immersed transformers.

Colour: grey; Thickness, 5 mils.

Kraft paper.—It is made from wood fibre and is practically a pure cellulose and is characterised by freedom from mechanical wood, sulphite pulp, bleaching or sizing material and other soluble salts. It has a highly calendered surface. It is used in small thicknesses for cable insulation and large thicknesses for layer insulation of coils.

Colour: brown; Thickness, 10 mils.

Glass.—Microscope cover slides of glass 1·2″ × 1·2″ × 4 mils. were used.

STUDIES IN DIELECTRICS.

PART II. THE EFFECT OF SUPERIMPOSED MAGNETIC FIELDS ON THE PERMITTIVITY AND POWER FACTOR OF DIELECTRICS.

By N. V. Narayanaswami and F. N. Mowdawalla.

The effect of superimposed magnetic fields on the permittivity and power factor of insulating materials is important from both physical and practical standpoints. An increase in the power factor would lead to greater dielectric losses and heating and this would, in the long run, result in a lower breakdown voltage of dielectrics, due to their consequent deterioration. On the other hand, a reduction of the power factor, and consequently the losses, would result in a more satisfactory functioning of the insulation and lead to longer life.

The literature relating to work in this direction is very meagre. Monkhouse (*Proc. Phys. Soc.*, 1928-29, **41,** 83) has conducted tests on pressboard under a "highest maintained A-C stress" in accordance with E.R.A. report A/S_2 (*Journal I.E.E.*, 1922, **60,** 794) and from the measurement of the temperature rise of the specimen and the time of breakdown, he concludes that the power factor and losses are considerably increased by a superimposed magnetic field. Measurements of dielectric losses in bakelised paper and glass by A. Smurrow (*Archiv. f. Elektrot.*, 1929, **22,** 31) showed that these are considerably affected by a unidirectional magnetic field. Fujikawa and Kitasato (*Bull. I.P.C.R.*, 1931, **10**, 153) have measured the power factor of pressboard, empire cloth, oil paper and mica under the action of unidirectional magnetic fields up to 8 000 gauss by more accurate bridge methods and observed that in brown pressboard, the power factor was increased by a small amount (2 to 4 per cent.). The change was slightly greater with stronger fields, and the magnitude of the electric stress had practically no effect. In black pressboard the corresponding changes were greater (from ·2 to 17 per cent.). In empire cloth, the magnetic field produced an increase in the power factor at low values of electric stress, but a decrease at higher values of stress. The same result was observed with oil paper and mica. In general, the change in power factor was determined by the magnitude of the electric stress and the magnetic field intensity. Further work has been carried out by the same authors (*Sc. Papers, I.P.C.R.*, 1932, **19**, 148) on the influence of alternating magnetic fields on the power factor of pressboard, empire cloth and mica. With alternating fields up to 25 000 gauss, they have observed, in general, an increase in the power factor of the materials, the increase being greater with increasing magnetic fields. It was also observed that with the same magnetic field, the ratio of power factor with the magnetic field to that without the field decreased with increasing values of the electric stress. Further, with a given strength of the electric and magnetic fields, the ratio decreased as the angle of time phase difference between the two fields increased from 0 to 90°.

The investigations of R. Schmid (*Ann. der Physic*, 1932, **14,** 809) on the effect of unidirectional magnetic fields up to 14 000 gauss on the loss angle of micanite paper, bakelised paper, paraffined paper, excelsior linen and mica give contrary results. He has observed that the loss angle in these dielectrics at 500 cycles remained unchanged under the action of both longitudinal and transverse magnetic fields. Very recently the loss angle and insulation resistance of transformer oil, paraffin oil, glass, paper and linen under longitudinal unidirectional magnetic fields up to 12 000 gauss have been measured by Konried (*Archiv. f. Elektrot.*, 1934, **28,** 154) at frequencies from 50 to 200 cycles and it was observed that the magnetic field had no effect on these for all values of electric stress up to the breakdown value.

The results of these few workers are conflicting and lead to no definite conclusion. In connection with the study of the various dielectric properties of insulating materials undertaken in these laboratories, it was decided to investigate the effect of magnetic fields on their permittivity and power factor. The following measurements were made with unidirectional magnetic fields up to a maximum of 18 000 gauss with the help of the electromagnet described in Part I.

EXPERIMENTAL.

Schering Bridge.—For the measurement of the capacity and power factor of the dielectrics, the high voltage Schering Bridge was employed. A full description of a similar bridge is given by Churcher and Dannatt (*World Power*, 1926, **5,** 238). The standard, loss-free, 100 $\mu\mu$F condenser was of the concentric cylinder type with air as dielectric. It was completely enclosed in a wooden box lined with earthed metallic lining. The diagram of connections of the bridge is shown in Fig. 1. A vibration galvanometer with a sensitivity of 30 mm. deflection per micro-ampere at one metre distance was used as detector. The bridge and galvanometer were separated from the high voltage apparatus by an earthed metal screen to avoid stray capacity effects.

At maximum values of R_3 (1 000 ohms) and C_4 (1 μF) the vibration galvanometer was responsive to a change of 1 in 1 000 or 0·1 per cent. in both R_3 and C_4. Consequently at these values the capacity and power factor could be measured to an accuracy of 0·1 per cent. This represents only the highest accuracy obtainable; in other cases where the bridge impedances were different, the accuracy was lower but never fell below 0·5 per cent.

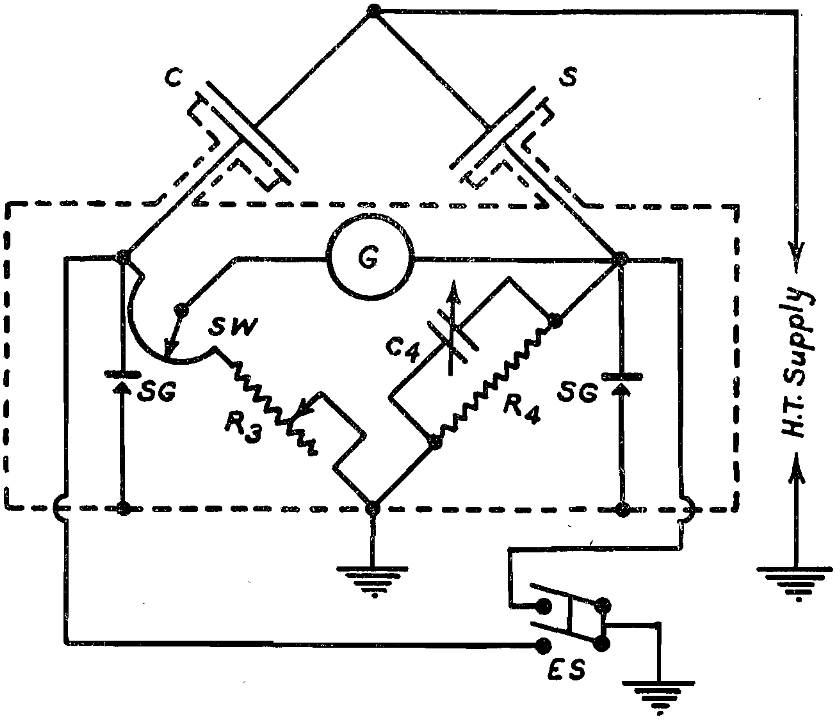

Fig. 1.

Schering Bridge.

C—Test condenser with guard-ring.
S—$100\mu\mu$F. Standard condenser.
R_3—Variable Resistance.
R_4—Fixed Resistance $= \frac{1000}{\pi}$ ohms.
C_4—Variable condenser.
G—Vibration galvanometer.
SW—Slide wire resistance.
- - - —Earthed screens.
SG—Safety gaps.
ES—Earthing switch.

Expressions for C, Cos φ and loss :—

$C = S.\frac{R_4}{R_3}\sin^2\phi$; $\cos\phi = \omega.C_4.R_4$.

Dielectric loss $W = \omega.C.E.^2 \cos\phi$, where,
E = applied voltage.
ϕ = phase angle of test condenser.
Correction for slide wire in series **with C is negligible.**

High Voltage Supply.—The test voltage was of 50 cycles and obtained from a 10 kVA, 220/115 000 V testing transformer supplied from a sine-wave alternator. The voltage and frequency of supply were completely under control.

Materials.—The following materials of which the dielectric strength under the action of unidirectional magnetic fields had been previously investigated (see Part I), were chosen for the tests; namely, Air, Transformer oil, Switch oil, Manilla paper, Presspahn, Pressboard, Kraft paper, and Glass. Mica was also tested. The materials were properly conditioned before the tests (see Part I, page 24).

Test Condensers.—The condenser used for the measurement of the permittivity and power factor of air and oil with longitudinal magnetic fields is shown in Fig. 2. It consisted of two 2″ diameter circular copper electrodes $\frac{1}{64}''$ thick pasted on two glass plates which formed the two sides of a small rectangular cell with an ebonite spacer between the glass plates. The distance between the electrodes was about $\frac{1}{16}''$. The capacity between the electrodes with air as dielectric was measured with the help of the Schering Bridge and found to be about 12 $\mu\mu$F. With the cell filled with oil, the capacity was about twice this value. For measurements with transverse magnetic field, a suitable condenser with large enough electrodes and capable of being accommodated in a short air gap was not available. Observations under this condition were therefore not possible.

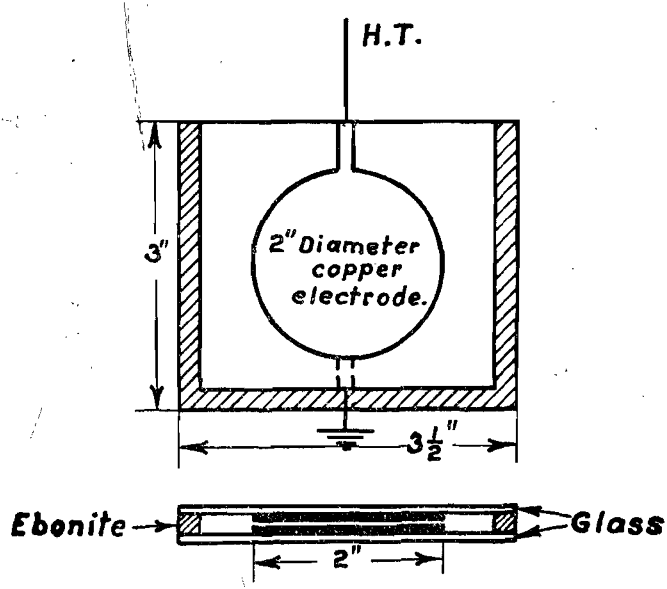

Fig. 2.

Condenser for the Measurement of Power Factor of Air and Oil with Longitudinal Magnetic Fields.

The test condenser for use with solid dielectrics under longitudinal magnetic fields consisted of two 1″ diameter brass discs, about $\frac{1}{64}$″ thick pasted on mica sheets (see Part I, Fig. 5). The dielectric under test was cut into 2″ square samples and held between the electrodes by means of four screws at the corners of the mica plates.

Fig. 3 represents the condenser used for measurements on solids with transverse magnetic field. The electrodes were 5 cms. × 4 mm. rectangular pieces cut out of $\frac{1}{16}$″ thick brass sheet and fixed to two ebonite pieces of the shape shown in the figure. The test samples cut to 6 cm. × 8 mm. rectangular pieces were held between the electrodes by two clamping screws at the top and bottom of the ebonite pieces. This condenser had a capacity accurately measurable on the bridge, and proved quite satisfactory.

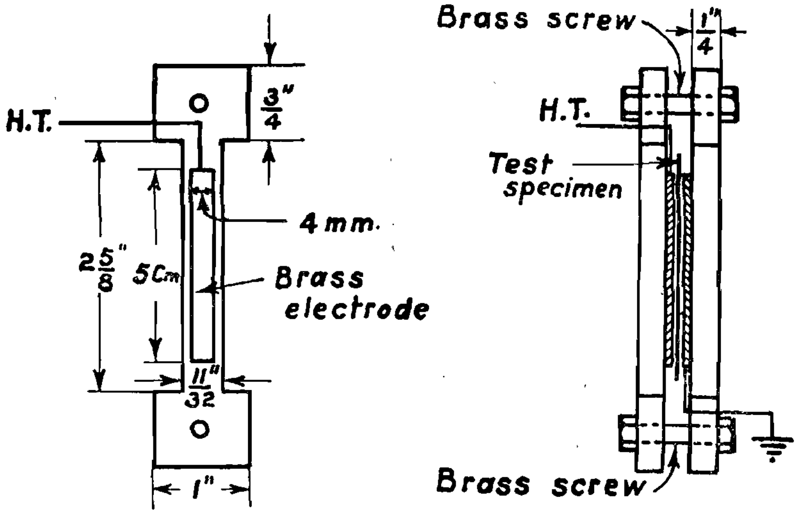

Fig. 3.

Condenser for the Measurement of Power Factor of Solids with Transverse Magnetic Fields.

Method of Testing.—The test condenser was placed in the air gap of the magnet and the electrodes connected to the transformer and bridge respectively. With the magnetic field off, measurements of capacity and power factor were made for both ascending and descending values of the electric stress; these were found to agree closely. The same measurements were repeated with the magnetic field. Beyond a certain value of the electric stress, the bridge became very unsteady and the measurements could not be continued. A large number of sets of readings were obtained for each material and the results reproduced here represent the mean values.

RESULTS.

All the results are given in Tables I to VII; some of them are also shown graphically in Figs. 4 to 7. C_e and $P.F_e.$ refer to values of capacity and power factor respectively without the magnetic field and C_{me} and $P.F_{me}.$ to those with the magnetic field.

TABLE I.

Air and Mineral Oils.

Longitudinal Magnetic Field: 15 000 Gauss.

Stress in kV per cm.		1·58	3·16	4·74	6·32	7·90	9·48	11·06	12·64
Air	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·000	—	1·000
	$P.F_{me}./P.F_e.$	1·000	1·000	1·000	1·000	1·000	1·000	—	1·000
Transformer Oil	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
	$P.F_{me}./P.F_e.$	1·000	1·000	1·000	1·000	1·000	1·000	0·990	1·000
Switch Oil	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·000	—	1·000
	$P.F_{me}./P.F_e.$	1·000	1·000	1·000	1·008	1·000	1·000	—	1·010

Table I shows that the permittivity and power factor of air and oil are unaffected by longitudinal magnetic fields up to 15 000 gauss. The slight changes at one or two points are probably due to experimental error. This result is in conformity with the observations of Konried (*loc. cit.*) who has detected no change in the loss angle of Transformer oil and glass with longitudinal unidirectional magnetic fields up to 12 000 gauss.

In the case of the solids, the measurements were made with both longitudinal and transverse magnetic fields. Tables II and III show that the permittivity and power factor of mica and glass are unaffected by both longitudinal and transverse magnetic fields, the few small discrepancies being probably due to experimental errors. These substances therefore resemble air and oil in this respect. The result agrees with that obtained by R. Schmid (*loc. cit.*) on mica and that by Konried (*loc. cit.*) on glass but differs from that of Fujikawa and Kitasato (*loc. cit.*).

TABLE II.

Glass.—Thickness, 50 mils.

Stress in kV per cm.		1·968	3·936	5·904	7·872	9·84	11·81	13·78	15·74
Longitudinal field 18 000 gauss	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
	$P.F_{me.}/P.F_{e.}$	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
Transverse field 12 500 gauss	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·010	1·010	1·000
	$P.F_{me.}/P.F_{e.}$	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000

TABLE III.

Mica.—Thickness, 3 mils.

Stress in kV per cm.		32·75	65·50	98·25	131·00	163·75	196·5	229·25	262·00
Longitudinal field 18 000 gauss	C_{me}/C_e	1·000	1·000	1·000	1·000	1·004	1·000	1·000	1·000
	$P.F_{me.}/P.F_{e.}$	1·000	1·000	0·995	1·000	1·000	0·996	1·004	1·004
Transverse field 12 500 gauss	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
	$P.F_{me.}/P.F_{e.}$	1·000	1·000	1·010	1·000	1·000	1·000	1·004	1·000

The other solid dielectrics, however, show distinct changes in power factor and slight changes in permittivity. The permittivity of manilla paper (Table IV, Fig. 4) is unaffected by the transverse field but is increased by about 1 per cent. by the longitudinal field. With the longitudinal field, its power factor increases by about 5 to 8 per cent. while with the transverse field, it decreases by about 1 to 2·5 per cent. The value of the electric stress also determines the magnitude of the change; the higher the electric stress, the greater is the observed effect of the magnetic field.

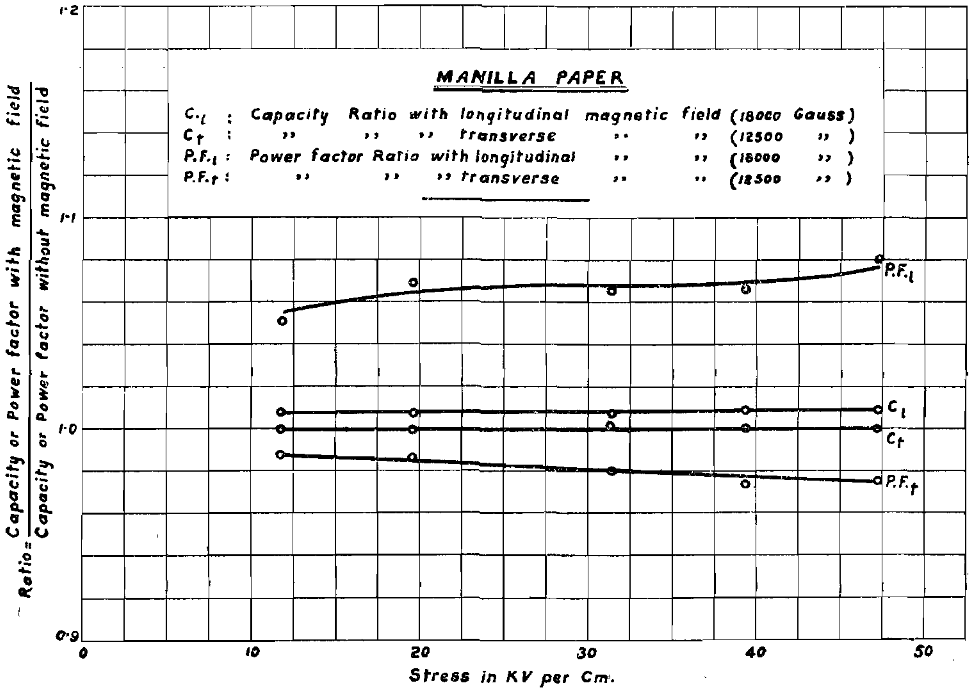

Fig. 4.

Variation of the Permittivity and Power Factor of Manilla Paper with Magnetic Field at Different Electrical Stresses.

(*Refer Table IV.*)

In presspahn (Table V, Fig. 5) the permittivity seems to be unaffected by the magnetic field but the power factor increases by about 10 per cent. with the transverse field and decreases by a similar amount with the longitudinal field. The curves indicate a maximum change at a particular value of the electric stress which is about 35 kV per cm. with the transverse field and 48 kV per cm. with the longitudinal field.

TABLE IV.

Manilla Paper.—Thickness, 5 mils.

Stress in kV per cm.		11·8	19·68	31·4	39·36	47·2
Longitudinal field 18 000 gauss	C_{me}/C_e	1·008	1·007	1·007	1·009	1·010
	$P.F_{me}/P.F_e$	1·051	1·070	1·066	1·066	1·080
Transverse field 12 500 gauss	C_{me}/C_e	1·000	1·000	1·000	1·000	1·000
	$P.F_{me}/P.F_e$	0·988	0·986	0·980	0·974	0·975

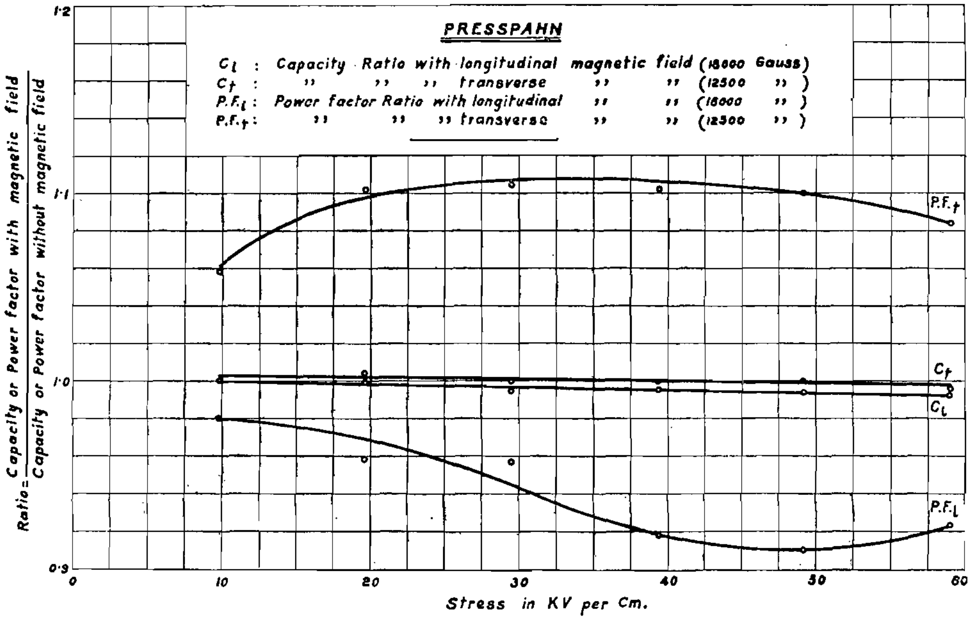

Fig. 5.

Variation of the Permittivity and Power Factor of Presspahn with Magnetic Field at Different Electrical Stresses.

(Refer Table V.)

TABLE V.

Presspahn.—Thickness, 10 mils.

Stress in kV per cm.		9·84	19·68	29·52	39·36	49·2	59·04
Longitudinal field, 18 000 gauss	C_{me}/C_e	1·000	0·999	0·994	0·996	0·994	0·992
	$P.F_{me}/P.F_e$.	0·980	0·958	0·957	0·918	0·910	0·923
Transverse field, 12 500 gauss	C_{me}/C_e	1·000	1·004	1·000	1·000	1·000	0·995
	$P.F_{me}/P.F_e$.	1·058	1·102	1.104	1·102	1·100	1·084

Pressboard (Table VI, Fig. 6) resembles presspahn in this that its permittivity is unaffected by magnetic fields. The behaviour of these two substances with regard to changes in power factor is, however, different. The longitudinal magnetic field produces an increase in the

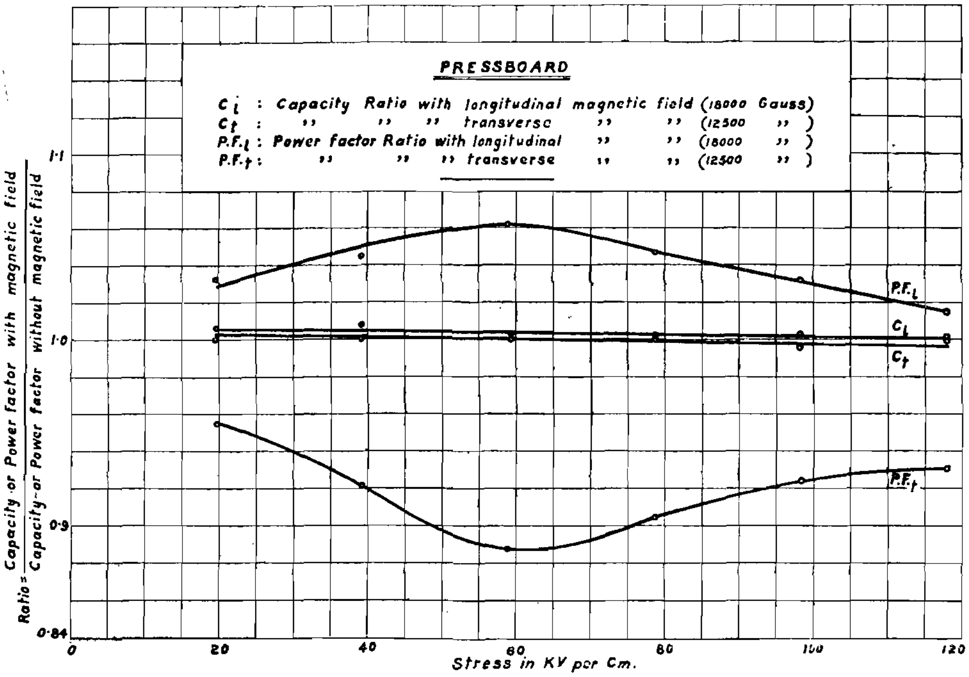

Fig. 6.

Variation of the Permittivity and Power Factor of Pressboard with Magnetic Field at Different Electrical Stresses.

(*Refer Table VI.*)

power factor of pressboard of up to 6 per cent. while the transverse field produces a decrease of up to 9 per cent. The points of maximum change are more conspicuous and occur at a stress of about 60 kV per cm. In comparing these results with those published by Fujikawa and Kitasato (*loc. cit.*) it must be remembered that their tests were conducted at lower values of the electric stress (up to 35 kV per cm.) and magnetic field strength (up to 8 000 gauss). With the longitudinal magnetic field, an increase in the power factor of about 2 to 4 per cent. in brown pressboard and of about 2 to 17 per cent in black pressboard was observed by them. Though the changes observed by them are in the same direction as those observed here, it is difficult to compare the results without a knowledge of the composition of the materials.

The change in the permittivity of Kraft paper (Table VII, Fig. 7) is as high as about 2 per cent. ; the transverse field increases it and the longitudinal field decreases it. On the other hand, both longitudinal and transverse fields decrease the power factor ; the effect of the latter is greater and amounts to as much as 13 per cent. with an electric stress of 50 kV per cm. The curves again exhibit points of maximum change which are, however, not quite coincident.

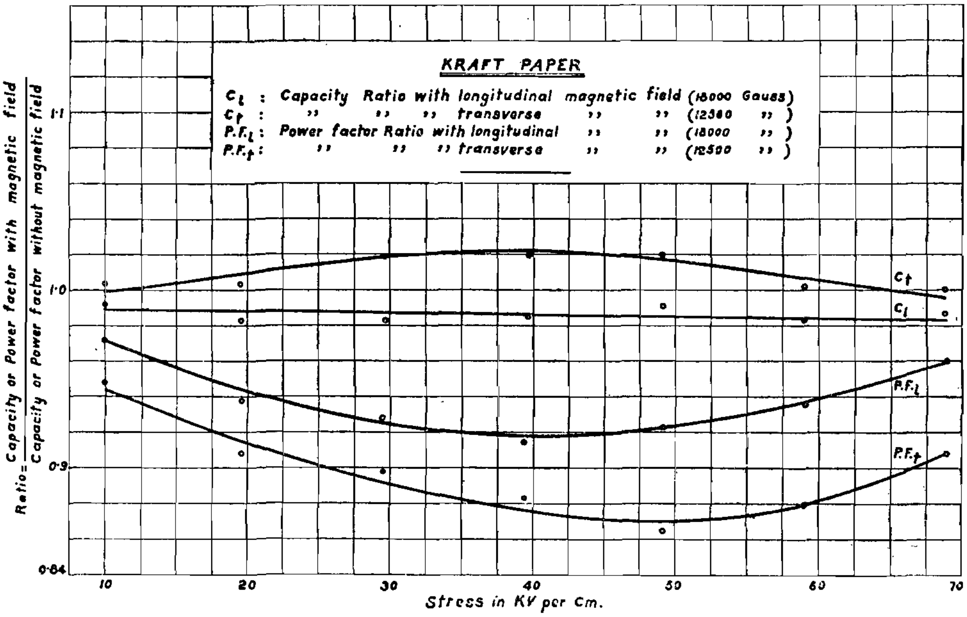

Fig. 7.

Variation of the Permittivity and Power Factor of Kraft Paper with Magnetic Field at Different Electrical Stresses.

(*Refer Table VII.*)

TABLE VI.

Pressboard.—Thickness, 5 mils.

Stress in kV per cm.		19·68	39·36	59·04	78·72	98·4	118·08	137·76
Longitudinal field 18 000 gauss	C_{me}/C_e	1·006	1·000	1·003	1·003	1·003	1·001	..
	$P.F_{me}./P.F_e.$	1·032	1·045	1·062	1·047	1·032	1·015	..
Transverse field 12 500 gauss	C_{me}/C_e	1·000	1·008	1·000	1·000	0·996	1·000	1·000
	$P.F_{me}./P.F_e.$	0·955	0·922	0·888	0·905	0·924	0·930	0·944

TABLE VII.

Kraft Paper.—Thickness, 10 mils.

Stress in kV per cm.		9·84	19·68	29·52	39·36	49·20	59·04	68·88
Longitudinal field 18 000 gauss	C_{me}/C_e	0·992	0·983	0·983	0·985	0·991	0·983	0·987
	$P.F_{me}./P.F_e.$	0·972	0·938	0·928	0·915	0·923	0·936	0·960
Transverse field 12 500 gauss	C_{me}/C_e	1·003	1·003	1·019	1·020	1·020	1·002	1·000
	$P.F_{me}./P.F_e.$	0·948	0·908	0·898	0·883	0·865	0·880	0·908

Comparing these changes with those produced by unidirectional magnetic fields in the B. D. V. of the same dielectrics (see Part I), it will be seen that in the case of manilla paper, pressboard and kraft paper, the change in power factor is of opposite sign to the change in B. D. V. In other words, a magnetic field, which increases the power factor and consequently the dielectric loss, reduces the B. D. V. of the material. If the final breakdown is due to temperature, this is what might be expected, because any factor increasing the dielectric loss would also increase the temperature rise and cause a breakdown at a lower value of dielectric stress. Similarly, a lowering of the power factor and the losses would tend to an increase in B. D. V. It must, however, be noted that presspahn behaves differently and consequently no general conclusion could be drawn from this result.

SUMMARY.

The effect of a superimposed unidirectional magnetic field on the permittivity and power factor of air, mineral oils and solid dielectrics has been studied and the following conclusions are drawn:—

(1) The permittivity and power factor of air and mineral oils are unaffected by longitudinal fields up to 15 000 gauss.

(2) The permittivity and power factor of glass and mica are not affected by longitudinal fields up to 18 000 gauss and transverse fields up to 12 500 gauss.

(3) The permittivity of manilla paper, presspahn, pressboard and kraft paper are very little affected by magnetic fields.

(4) Magnetic fields have an appreciable effect on the power factor of manilla paper, presspahn, pressboard and kraft paper, the nature and magnitude of the change depending on the relative directions of the magnetic and electric fields and the magnitude of the electric stress.

(5) The effect of the magnetic field appears to be maximum, in some materials, at a certain value of the electric stress.

(6) The change of power factor in manilla paper, pressboard and kraft paper is opposite to the change in their B. D. V. under similar conditions. In presspahn, however, the changes are in the same sense.

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RADIO FIELD INTENSITY MEASUREMENTS AT BANGALORE DURING THE POLAR YEAR.

By P. L. Narayanan.

SUMMARY.

The paper relates to the measurement of field intensities of received radio signals of low and medium frequencies.

Abnormal polarisation and deep fading during the dark hours and characteristic intensity variations in the neighbourhood of sunset and sunrise are the chief features of transmissions from Madras on 75 kc/s. The partial solar eclipse on 21st August 1933 caused a definite decrease in the value of the field intensity followed by a gradual rise after the middle of the eclipse.

The intensity curves of the long wave stations of Rugby, 16 kc/s, and Nauen, 16·54 kc/s, show a hump between 0600 and 0700 I.S.T.

Transmissions from Bombay and Colombo broadcasting stations are characterised by violent intensity changes during the night. The nature of the interference by foreign stations with Bombay and Colombo has been indicated.

INTRODUCTION.

The measurement of the intensity of radio signals from near or distant transmitting stations has a two-fold object. It helps to determine the minimum power required in the transmitting antenna for obtaining intelligible signals at different distances under specified physical conditions of transmission. It also throws considerable light on the nature of the propagation of radio waves round the earth.

OBSERVED STATIONS AND SIGNALS.

The present measurements relate mainly to the radio telegraph transmitter (VWO) at Madras working on 75 kc/s and the broadcast transmitter (VUB) at Bombay working on 840 kc/s. Occasionally, measurements have also been made on the signal intensity of the 700 kc/s broadcast transmitter at Colombo ; and, whenever practicable, the intensities of the radio telegraph transmitters at Nauen (DFY, 16·54 kc/s) and at Rugby (GBR, 16 kc/s) have also been recorded. Through the courtesy of the Director of Wireless, it was possible to arrange for special transmissions from Madras, from April to August 1933, consisting of continuous dashes of five minutes' duration, every Wednesday night from about 2200 to 0800 I. S. T. to facilitate accurate observations. Other measurements were made during the working hours of the stations concerned.

PRINCIPLE OF MEASUREMENT.

The procedure adopted in all cases was essentially the same. The signal from the required station was received on a suitable frame aerial with its plane in the direction of propagation. After tuning by a variable air condenser, the signal was passed through a suitable amplifier, the gain of which could be adjusted to the point of self-oscillation. The amplified signal was then rectified by an anode bend rectifier. In the output circuit of the latter was connected a Cambridge thread recorder giving half minute marks on a chart fixed on a drum driven by clock work. By adjusting the gear ratio, it was possible to revolve the drum at the rate of one revolution in 25 hours or in one-twelfth of that interval. Calibration of the receiver was effected by a local oscillator, tuned to the signal frequency, from which accurately known adjustable output voltages were obtainable. From the calibration curve of the receiving apparatus and the constants of the aerial circuit, the recorder chart was calibrated in terms of microvolts per metre of the incoming signal.

LOW FREQUENCY MEASURING APPARATUS.

Fig. 1 shows the diagram of connections used for the 75 kc/s signals from Madras. A similar equipment was used for observations on signals from Rugby and Nauen. These follow the method first used by Hollingworth (*Jour. I.E.E.*, 1923, **61**, 501).

Aerials.—The receiving aerials consisted of two separate square frames with sides 1·8 metres long, wound over with 7/22 stranded copper conductor. The spacing between adjacent turns was obtained by means of specially designed porcelain combs located at the four corners. The coil used for Madras had 20 turns and a measured inductance of 1500μH, while the other one had 50 turns and a measured inductance of 7650μH.

Receivers.—The receiver, housed in a screening aluminium box, consisted, in either case, of a three-stage capacity-resistance coupled amplifier with a variable condenser of 100$\mu\mu$F between the grid of the first triode and part of the anode resistance of the second for purposes of reaction control. The last triode acted as the rectifier. A pair of phones T was connected across the secondary of the transformer in the anode circuit of the rectifier for preliminary tuning. The rectified current was fed into the automatic recorder whose initial deflection in the absence of a signal gave the datum line for the record.

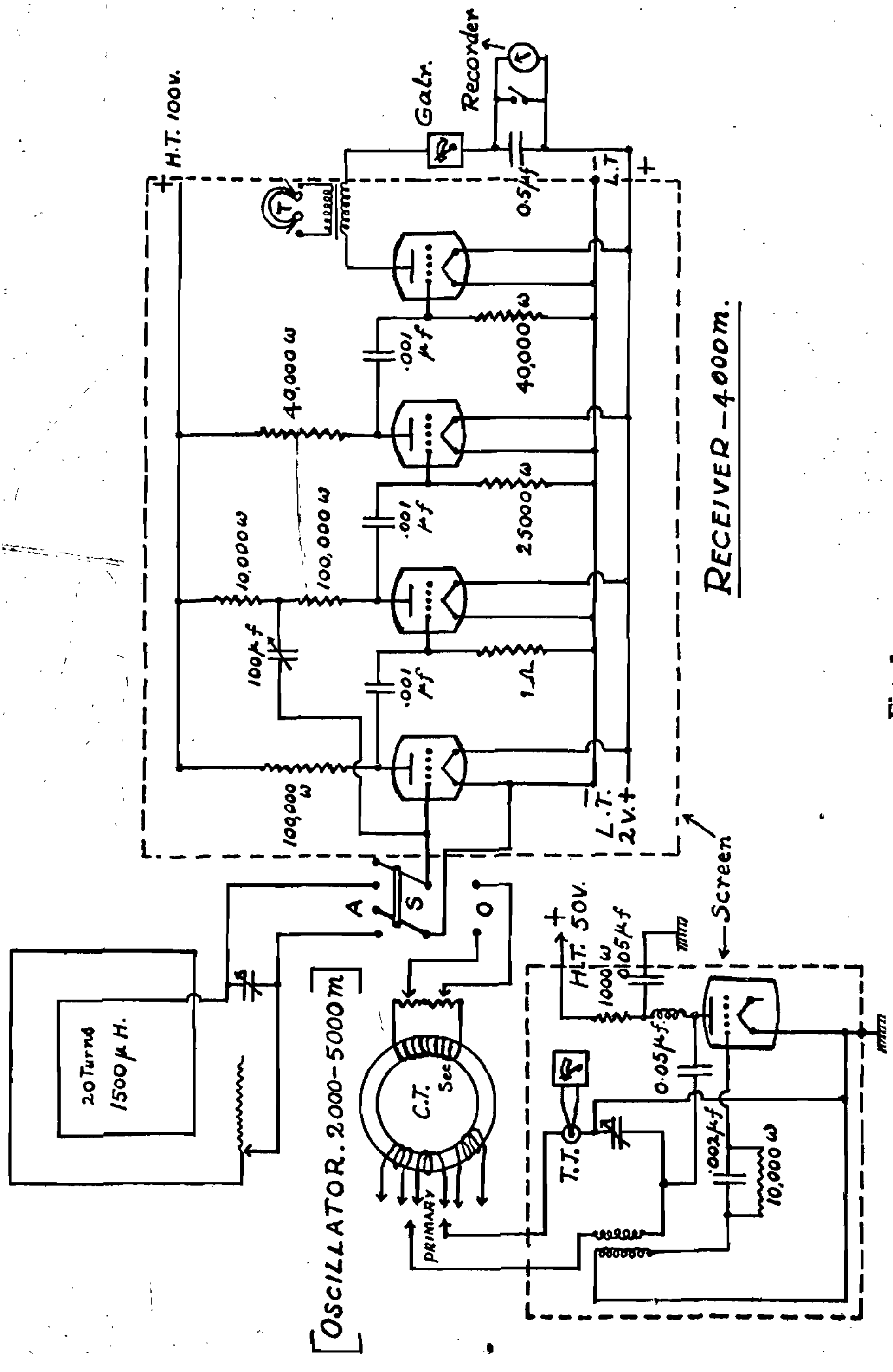

Fig. 1.
Low Frequency—Measuring Equipment.

Calibrating equipment.—The calibrating arrangement consisted, in each case, of a shielded oscillator. The oscillatory circuit included a thermo-junction T.J. and a current transformer C.T. (Dye, *Jour. I.E.E.*, 1925, **63,** 597) having a variable primary winding and a secondary winding of 100 turns. A radio frequency potential divider of 20 ohms resistance was connected across the secondary; knowing the primary current, the number of turns of primary winding and the potentiometer resistance, the output voltage could be easily calculated.

Method of operation.—The voltage developed by a field intensity F in a coil of area a, number of turns n, inductance L and effective resistance R is $\frac{2\pi an\omega L}{\lambda R}F$, where $\frac{\omega}{2\pi}$ is the frequency, and λ the wave-length of the incoming signal. This voltage after being amplified and rectified produces a deflection in the recorder. The object of calibration is to measure the voltage which would produce the same deflection as the incoming signal. The double throw switch S is thrown over to the oscillator and deflections are obtained in the recorder corresponding to a number of input voltages, by varying the potentiometer resistance. The current in the oscillatory circuit and the ratio of the primary to the secondary turns remaining the same, the input voltages are proportional to the corresponding potentiometer resistances. From the curve connecting the input voltage and the deflection produced by it, the signal voltage corresponding to a known deflection can be obtained. The frequency of the signal and the constants of the aerial being known, the signal intensity can be calculated if R is determined.

R is the effective resistance of the entire aerial circuit and is considerably influenced by the reaction control condenser. For the determination of R, the resistance variation method was adopted on account of its simplicity. The observations were made sometimes on the incoming signal and on other occasions on a local signal tuned exactly to the frequency of the former; in the latter case, the plane of the aerial was set perpendicular to the direction of transmission to cut out the distant signal as far as possible.

Precautions.—As the receiving equipment was intended to be in continuous operation for long hours it was essential that the set should be perfectly steady in operation and free from any tendency towards instability even under the worst conditions of atmospheric disturbances. The reaction condenser was therefore set below the point of instability, but at a position to give satisfactory deflections in the recorder at all hours. After the preliminary observations had been made, the telephones were disconnected as, otherwise, the receiver was found to be unstable.

MEASUREMENTS ON MADRAS.

The observations on the Madras transmissions indicate that, in general, while the signal strength remains more or less constant during the day time, it is subject to violent fluctuations after sunset and throughout the dark hours of the day. It can be seen from the movements of the recorder needle that the signals at night are very

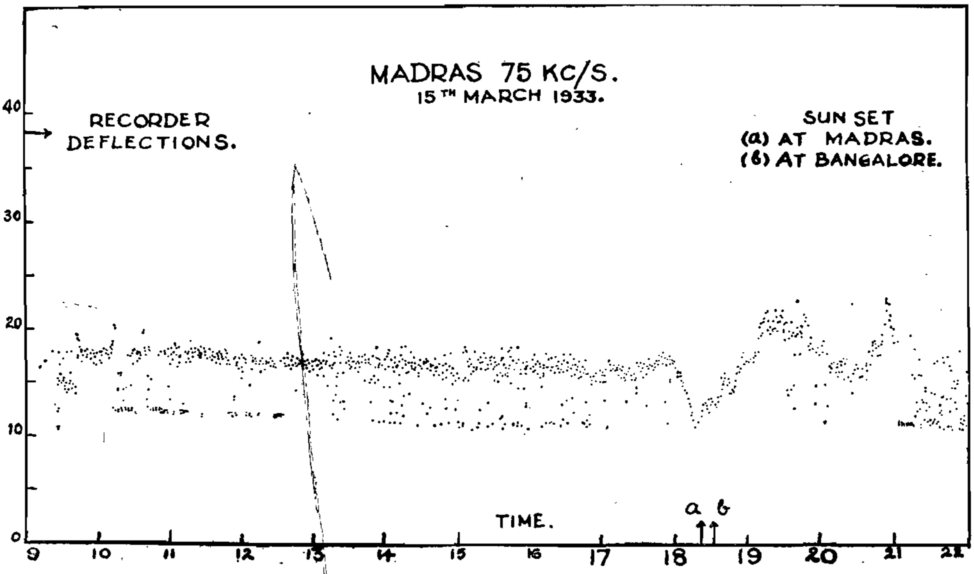

Fig. 2(a).

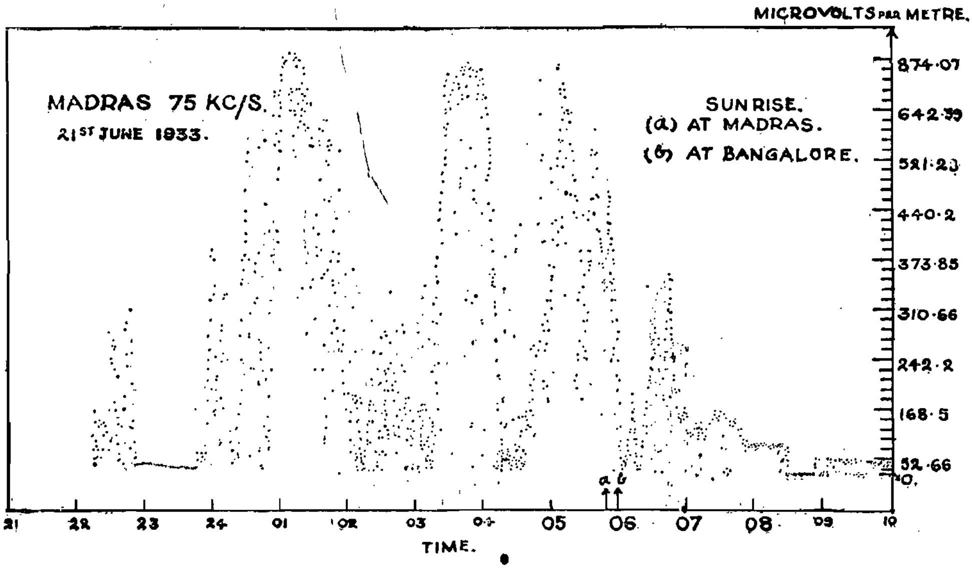

Fig. 2(b).

unstable and are subject to considerable variations within a fraction of a minute. The presence of this rapid and deep fading at the low frequency of 75 kc/s is noteworthy. At sunset there is usually a sudden well-defined dip in the intensity curve, the minimum value coinciding more or less with the time of sunset. This dip is the starting point of fluctuations during the night hours. At the hour of sunrise there is another sharp dip in the intensity curve coinciding more or less with the hour of sunrise. While similar dips occur at random at all hours of the night it is invariably present at the hour of sunrise. These dips in the intensity curves can be seen in Figs. 2a and 2b.

The average value of the intensity during the day and night hours has been calculated and shown in Fig. 3. The average day values have been worked out for the period 0800—1700 I.S.T., and the night values for 2000—0500 I.S.T. These hours do not include the time of sunrise and sunset and therefore the averages are free from the varying influences due to these. These mean values have been derived from the 24-hour charts recorded on Wednesdays from April to August 1933. The dotted lines in the graph indicate the absence of transmission or the breakdown of the recording equipment.

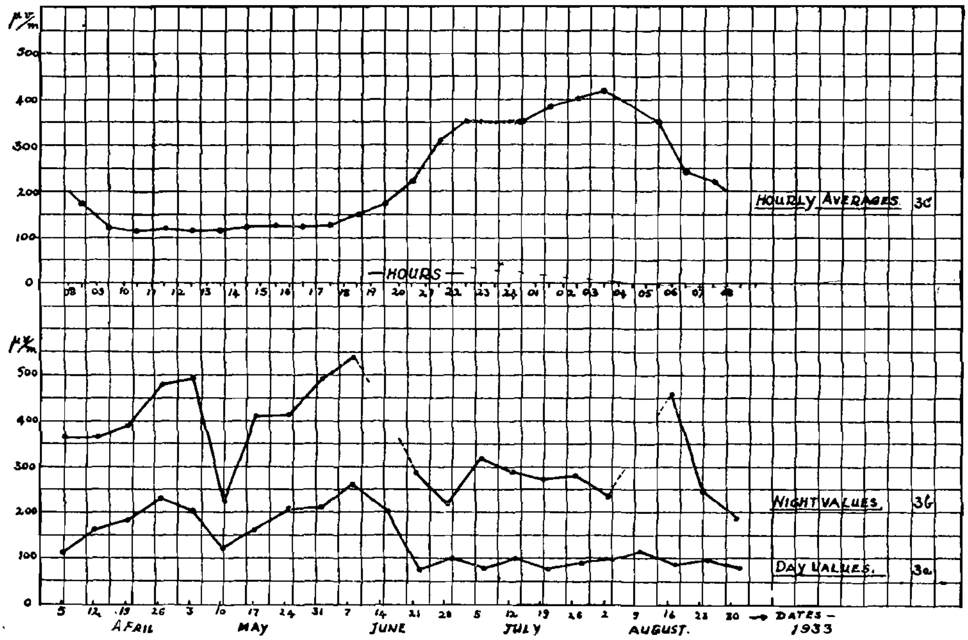

Fig. 3.

Average Intensity Curves.

Fig. 3a, for the average day value, indicates a considerable variation in intensity during April and May and a very much smaller variation in June, July and August. The variations during the night as indicated by 3b are much greater than the day values. The mean of the night values (325 μv/metre) is nearly three times the mean of the day values (121 μv/metre). The observations on the special transmissions alone gave the mean average night value of 387 μv/metre for the field intensity of Madras at Bangalore. These may be compared with the signal intensities calculated from the Austin-Cohen's and Fuller's formulæ. Taking the usual current of 50 amperes in the transmitting aerial and assuming the effective height of the aerial to be half the geometrical height (80·47 metres), the intensities calculated from these formulæ are respectively 527 and 543 μv/m.

Fig. 3c shows the hourly average values of signal strength over the entire period and indicates more clearly the difference in the signal strengths between the day and night hours. It also shows the comparative constancy of intensity during the day hours and the large fluctuations at night.

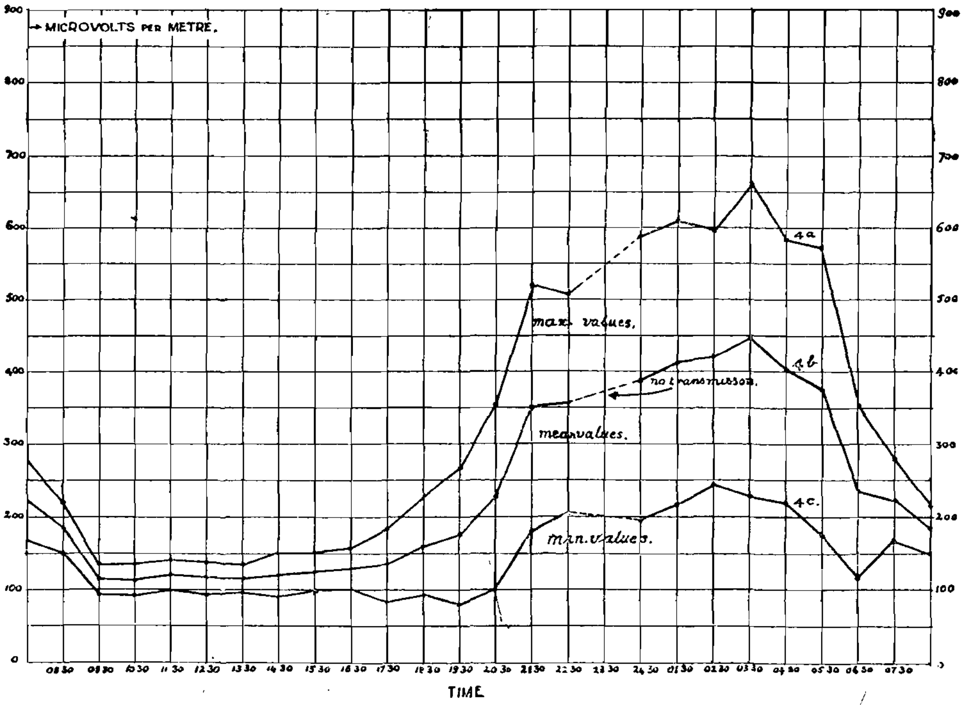

Fig. 4.

Hourly Intensity Curves.

Curves a and c in Fig. 4 show the average of the maximum and minimum values of intensities occurring during each hour taken over the whole period. Fig. 4b represents the mean of these curves. The width of the ordinate between 4a and 4c at any point indicates the extent of the variation of the signal at that hour. The ratio of the mean variation to mean intensity is about three times as great during night as during day.

Abnormal polarisation.— Fig. 5a is the record of the signal with the axis of the receiving frame aerial parallel to the direction of transmission. From the commencement of transmission at about 1000 till 1745, there is no deflection in the recorder. This indicates that during these hours the electric vector of the down-coming wave has no component perpendicular to the plane of propagation. As the time of sunset approaches the recorder needle begins to move and the deflection rapidly increases to a maximum at about 1910. The sky wave undergoes a rotation of its plane of polarisation, giving rise to a component of the electric vector perpendicular to the plane of propagation. That this abnormal component is not constant in intensity and that it fades almost as severely as the component in the plane of propagation are shown on the two figures between the hours 1900 and 2300.

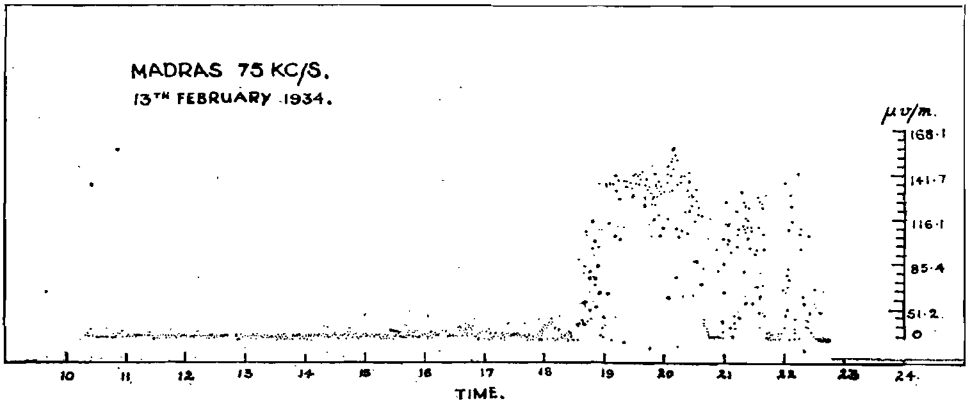

Fig. 5(a).

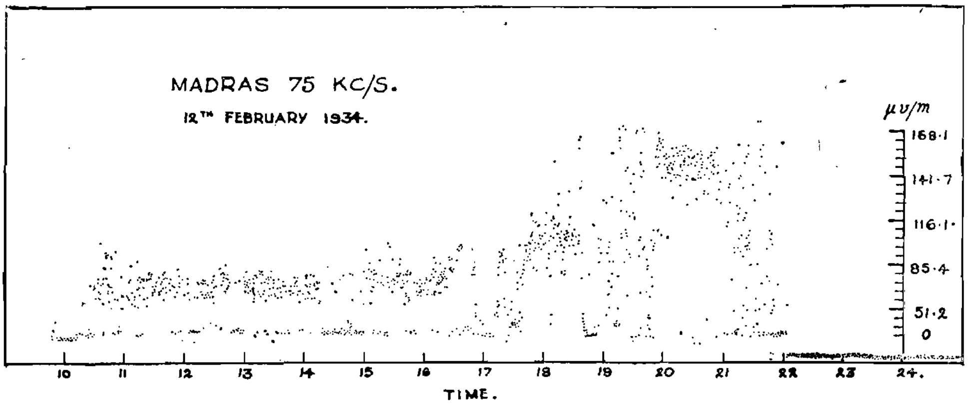

Fig. 5(b).

While the absence of any deflection between 1000 and 1700, with the coil in the broadside-on position shows that the electric vector of the down-coming wave is entirely in the plane of propagation, the constant deflection between the same hours with the coil in the end-on position, as shown in 5b, is evidence of the constancy of its intensity during this period. It is only towards sunset that its intensity and plane of polarisation begin to change. During the period of darkness both the normally and abnormally polarised components are strong and undergo violent and rapid changes in intensity.

In Fig. 6 are shown two curves representing the signal strengths between 1750 and 1950, obtained simultaneously on two different

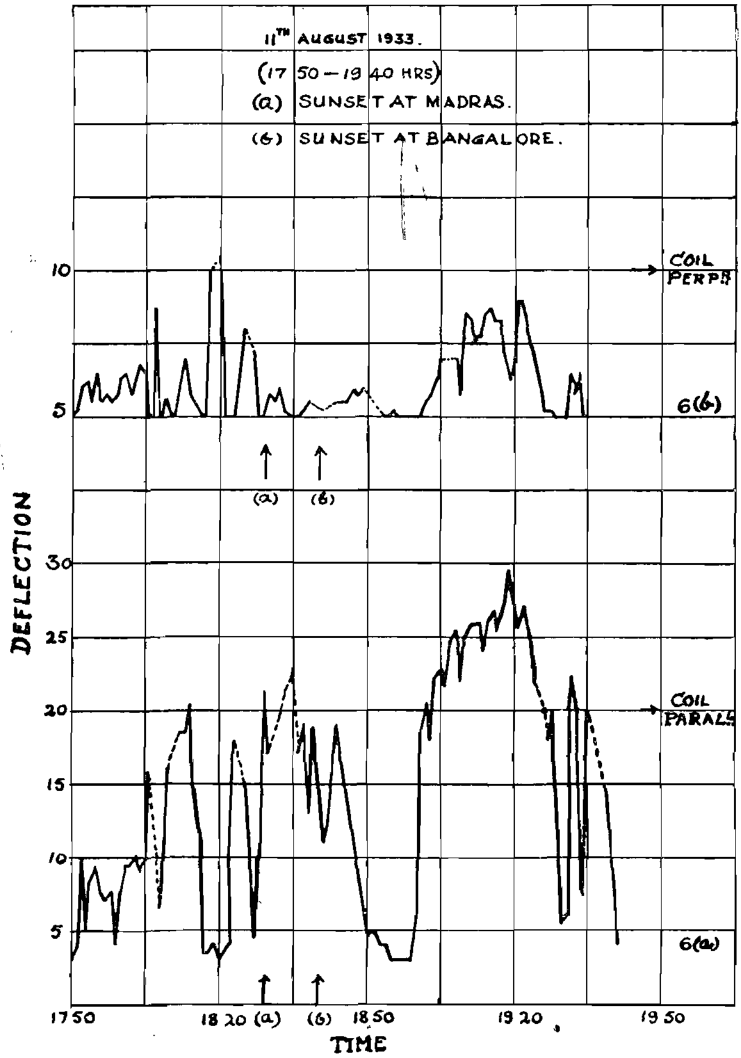

Fig. 6.

receivers with their coil aerials parallel and perpendicular, respectively, to the plane of transmission. The ordinates are not to the same scale. Between 1817 and 1827 there seems to be a change in the plane of polarisation, while from 1850 to 1930 the plane of polarisation appears to have changed but little, while the intensity has varied considerably.

Effect of the Solar Eclipse.— Fig. 7a shows the intensity

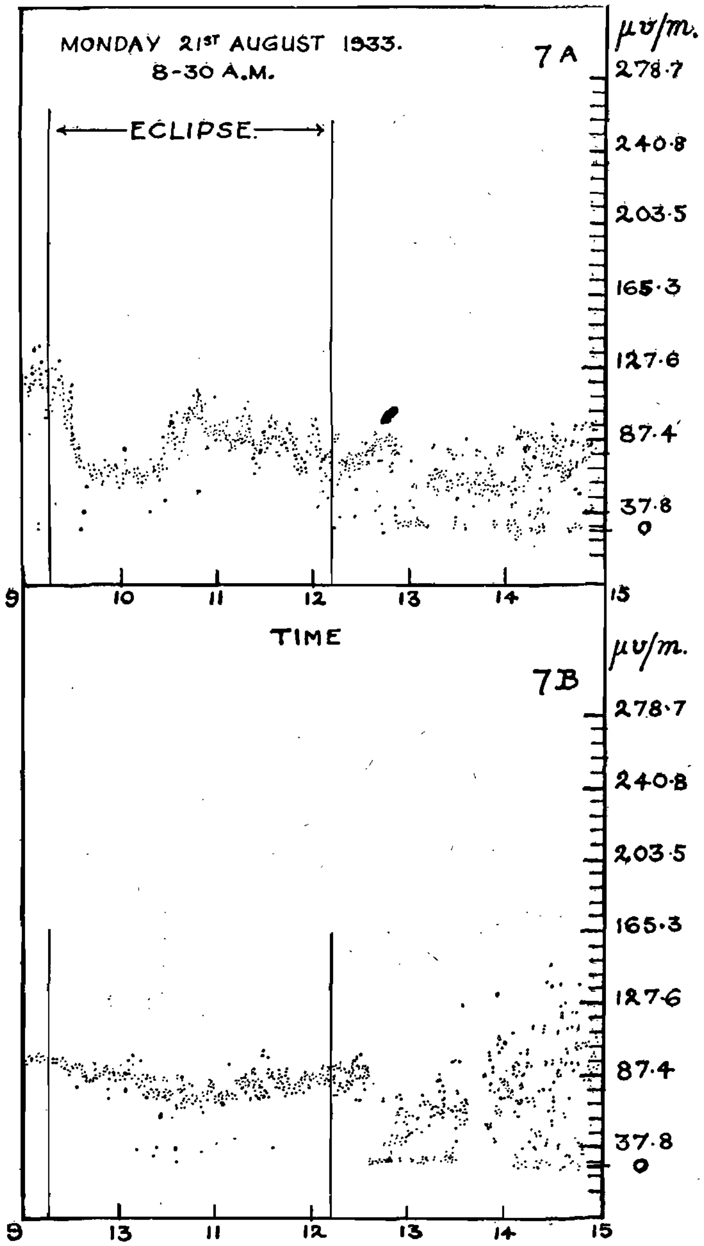

Fig. 7.

variations of Madras during the partial solar eclipse on 21st August 1933, and Fig. 7b shows a record taken on the following day for the purpose of comparison. There is a small but definite decrease of intensity during the first half of the eclipse, followed by a gradual increase during the second half.

Observations made on medium wave-lengths in England during the eclipse of 29th January 1927 (*Jour. I.E.E.*, 1928, **66**, 876) and in America on 24th January 1925 (*Proc. I.R.E.*, 1925, **13**, 539) show a rise instead of a fall in the intensity charts during the first half of the eclipse.

MEASUREMENTS ON RUGBY AND NAUEN.

Atmospheric disturbances on these wave-lengths are very severe and often cause instability in the receiving set. Sensitivity had, therefore, to be sacrificed in order to secure stable working. The intensity variations of the low frequency distant stations are much less prominent than those of the 75 kc/s transmissions from Madras. However, an interesting feature is a gradual increase and fall of the intensity between 0600 and 0700 appearing as a hump which can be seen on the chart for Rugby shown in Fig. 8.

MEASUREMENTS ON BOMBAY AND COLOMBO BROADCAST STATIONS.

The arrangement and operation of apparatus for measuring the signal intensities of the broadcast stations at Bombay and Colombo are, in principle, the same as for low frequencies. Fig. 9 gives the diagram of connections.

Aerial.—The vertical frame aerial had an area of about 1·4 sq. metres and consisted of 6 turns of 7/22 stranded copper wire wound over porcelain combs fixed at the corners of the frame.

Receiver.—The receiver had two transformer coupled screen grid stages for radio frequency amplification; the third was a triode for rectification and the fourth a pentode for amplifying the audio frequency output from the rectifier. Each stage was screened from the other by suitable partitions. Any tendency to instability was prevented by reducing the filament current or altering the bias by the potentiometer P. Small signal intensities of the order of 3 to 5 μv/m. could be recorded without risk of self-oscillation.

Calibrating equipment.—The calibrating oscillator was similar to those used for the low frequencies, but the output was taken from a small coupling coil C with a thermo-junction T.J. and a radio frequency potential divider R.

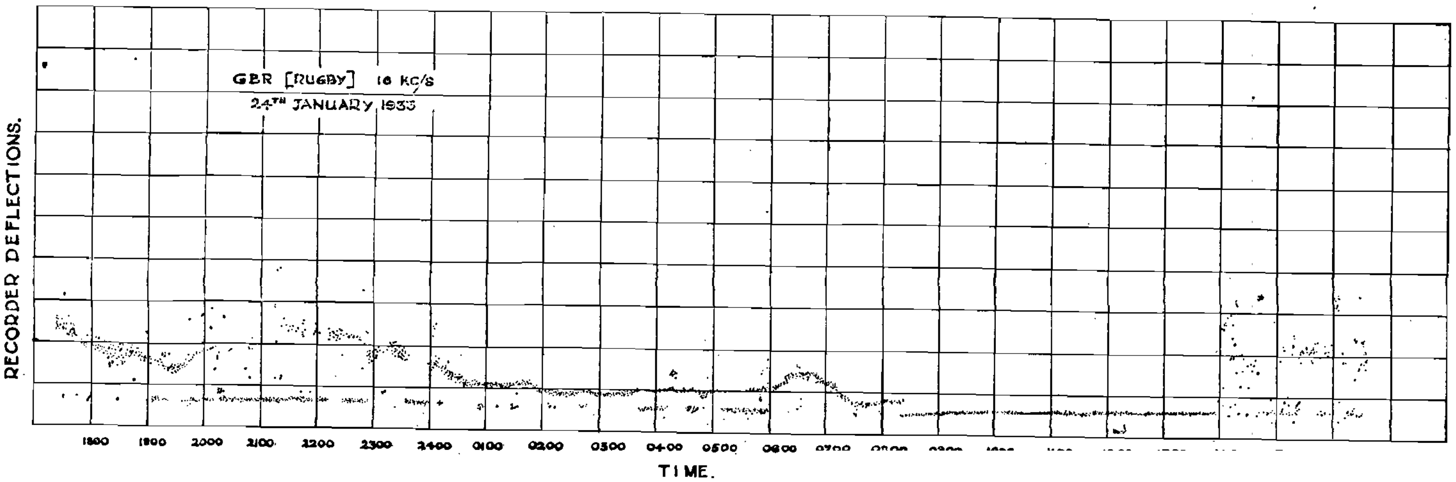
GBR [RUGBY] 16 KC/S
24TH JANUARY 1933
RECORDER DEFLECTIONS.
1800
1900
2000
2100
2200
2300
2400
0100
0200
0300
0400
0500
0600
0700
TIME.

Fig. 8.

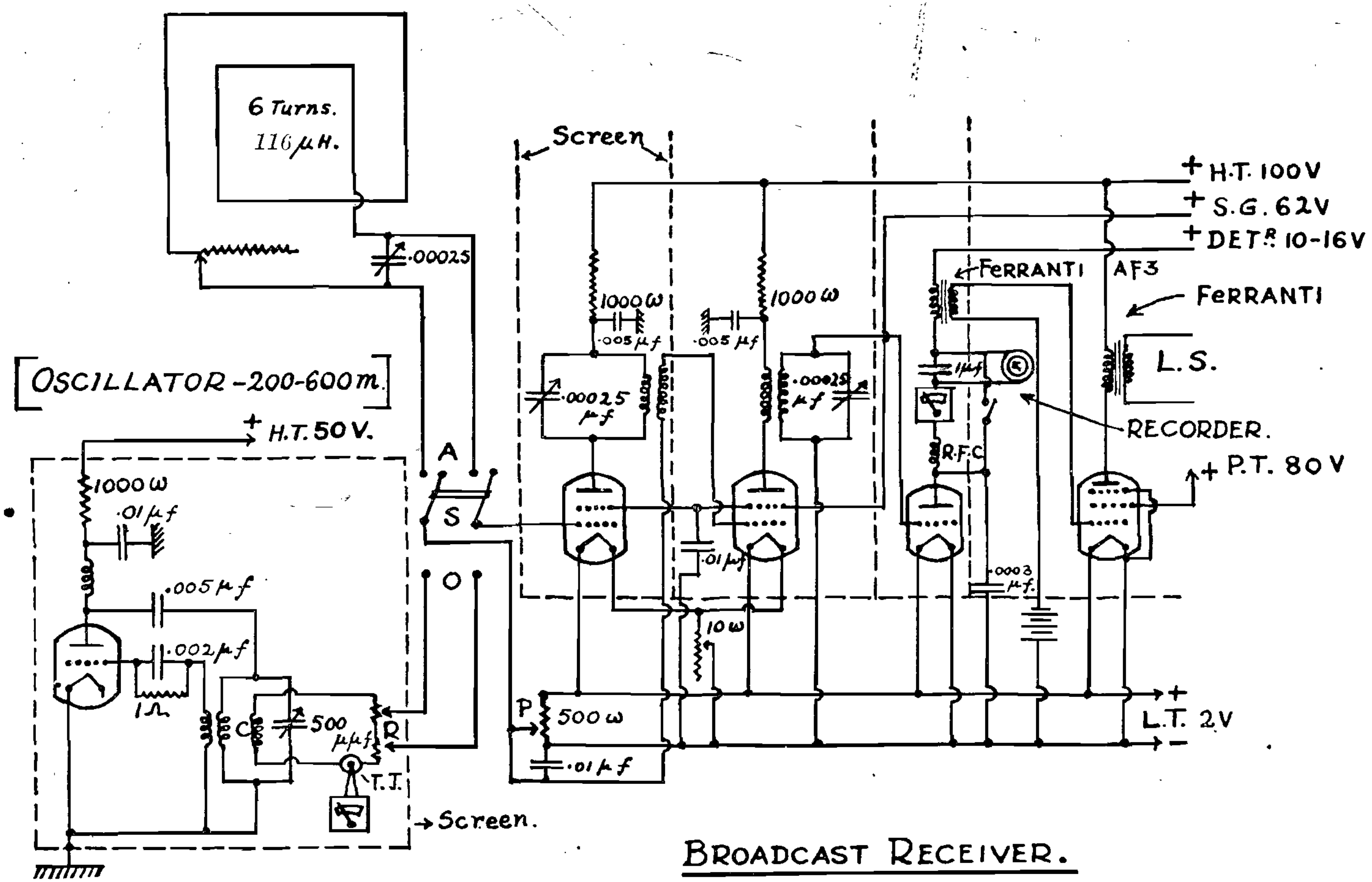

Fig. 9.

Medium Frequencies—Measuring Equipment.

Procedure.—The method of operation and measurement was exactly the same as that for low frequency observations. As both laboratory and atmospheric disturbances affected smooth working, sensitivity had to be sacrificed a little in order to secure stability. The routine programmes from the transmitting station constituted the signal and, as this was generally unsteady, measurements of effective resistance were carried out on a local signal tuned exactly to the frequency of the station.

Results of observations.—Fig. 10a gives the signal intensity variations of the Bombay broadcasting station. It shows the deep and rapid fading of the Bombay transmissions at Bangalore, a change from zero to maximum often occurring within the short period of 30 seconds. The actual deflections of the recorder indicated that the fading was often of shorter duration. When the aerial was rotated about the vertical axis and kept at various positions the minima obtained were never sharp nor steady. A three hours' record, obtained with the plane of the aerial perpendicular to the direction of transmission, is shown in Fig. 10b. This shows that the horizontal electric vector of the down-coming ray is also subject to violent fluctuations of intensity.

The mean average value of the intensity recorded between the hours 2100 and 2300 during the months of July, August and September is 87·5 $\mu v/m$ and is shown on Fig. 11. During the day the transmissions from Bombay can be heard but faintly on infrequent occasions. It has never been possible to observe the signal on the recorder.

A record of the Colombo transmissions is shown in Fig. 12. Fading is as severe as with the Bombay transmissions. During the day this station has been heard on the receiver when adjusted to a sensitive condition. The average intensity recorded during the months of January and February was 70 $\mu v/m$ between 1930 and 2030. The day intensity is too low to be recorded with any accuracy.

Interference.—Both Bombay and Colombo stations were affected by interference from foreign stations. After about 2030 when Bombay* was tuned in, a continuous whistling was heard. The whistle varied in intensity and when it increased a European station was heard faintly in the background. With a local oscillator, the frequency of the interfering station was found to be slightly lower than that of Bombay. It was heard either when Bombay was on or when the local oscillator was working. It was not possible to measure the intensity of the foreign station.

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* Bombay has recently changed from 840 kc/s to 855 kc/s and the transmissions appear still to be affected by interference.

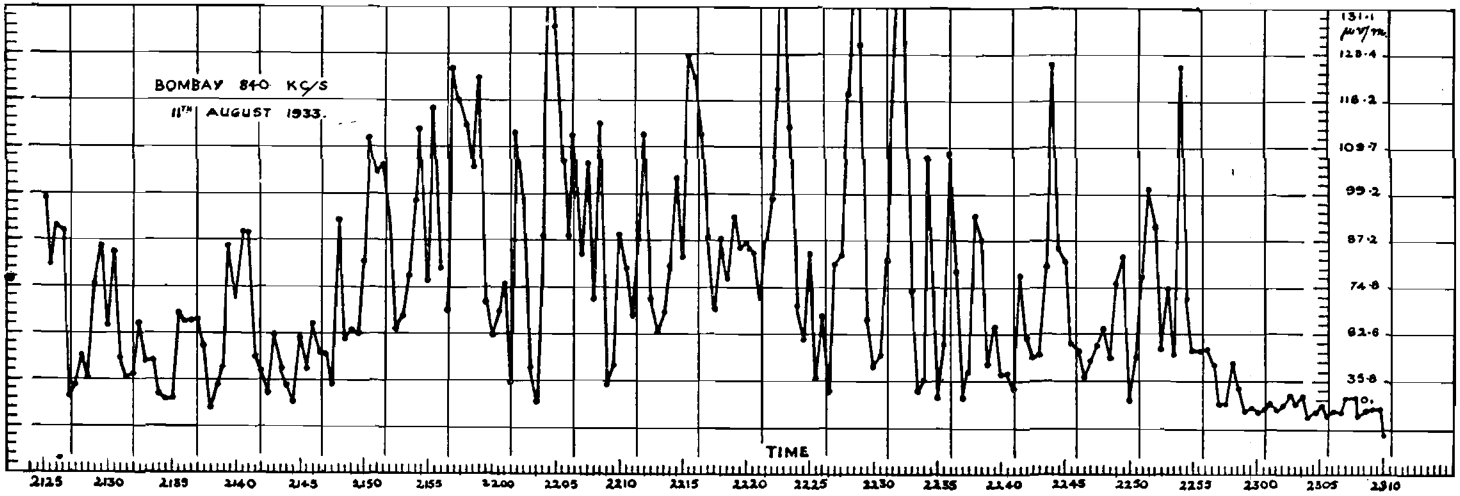
BOMBAY 840 KC/S
11TH AUGUST 1933.
131·1
μV/m.
128·4
116·2
109·7
99·2
87·2
74·8
62·6
35·8
0.
TIME
2125
2130
2135
2140
2145
2150
2155
2200
2205
2210
2215
2220
2225
2230
2235
2240
2245
2250
2255
2300
2305
2310

Fig. 10(a).

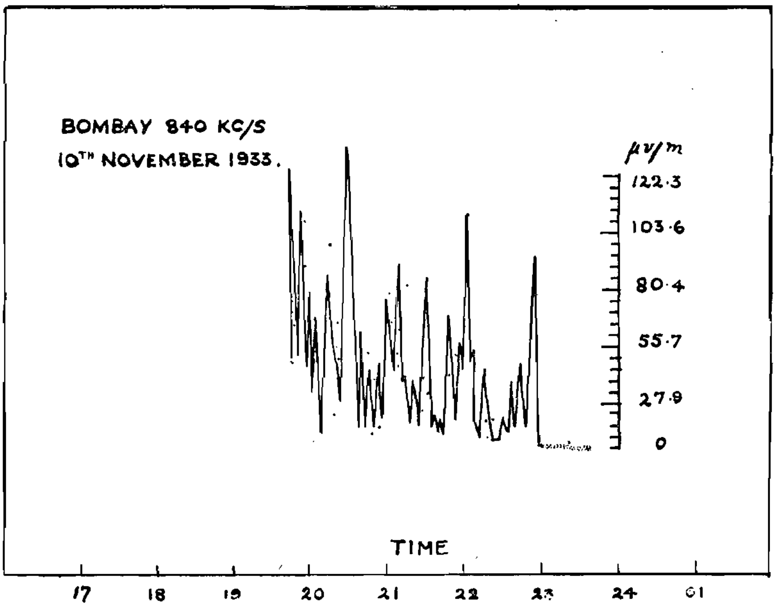

Fig. 10(b).
Coil Perpendicular to Direction of Propagation.

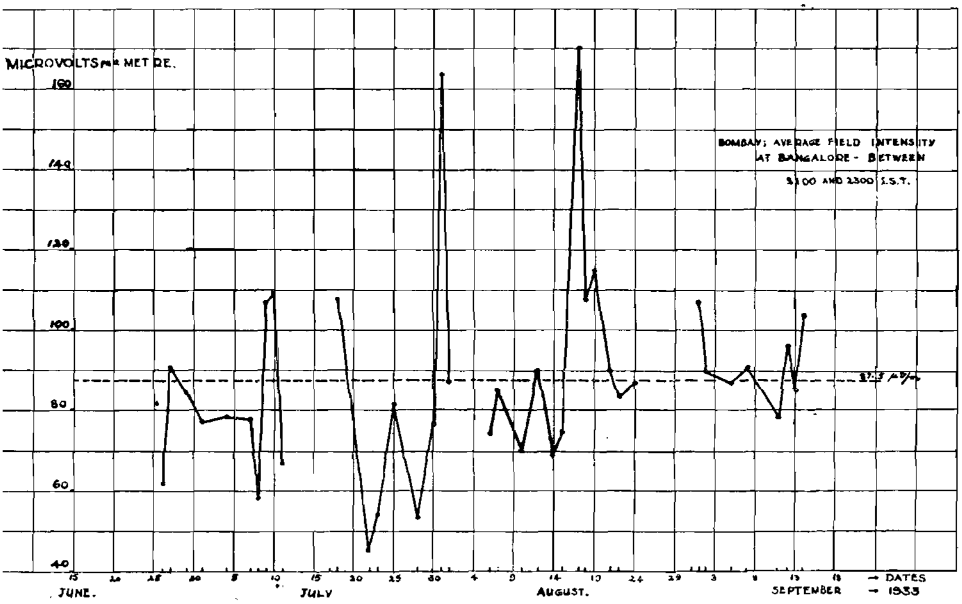

Fig. 11.

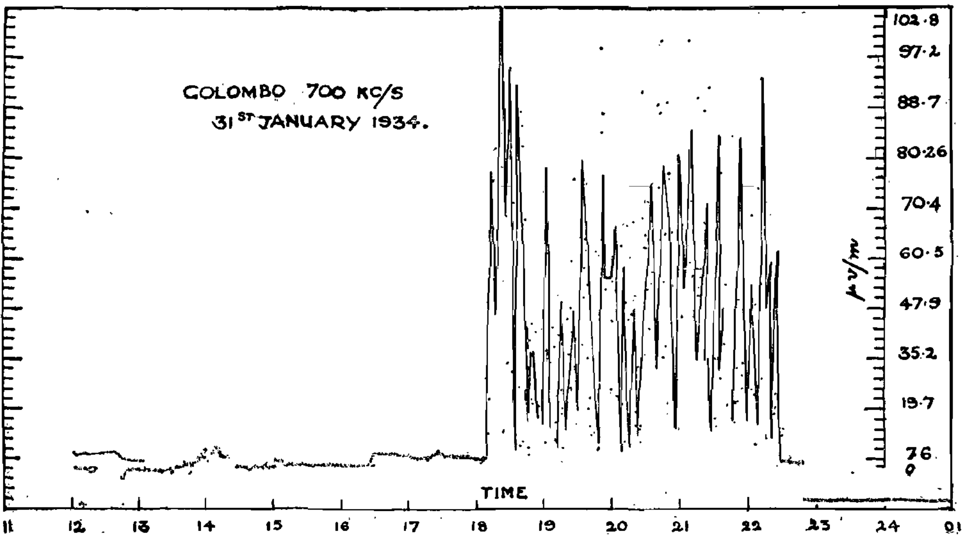

Fig. 12.

While it was sometimes possible to get Bombay free from the interfering station by increased reaction on the receiver, Colombo could not be separated out from the foreign station; but the weak interfering signal could often be suppressed by making the set less sensitive. This suggests that the station interfering with Colombo has the same or a harmonic frequency corresponding to that of Colombo.

CONCLUSION.

The above relates to part of the programme of work undertaken during the Polar Year 1932–1933. My best thanks are due to Mr. K. Sreenivasan for his valuable guidance and help at every stage of the work. Thanks are also due to the Director of Wireless with the Government of India, for kindly arranging special experimental transmissions from Madras. To Prof. F. N. Mowdawalla my thanks are due for his interest in the work and the discussion of the results.

APPENDIX I.

The following table gives the details of the stations on which observations were taken :—

Station	Call Sign	Working Wave-length	Location	Great Circle Distance from Bangalore	Bearing from Bangalore
Bangalore	..	..	12°–57′N 77°–35′E	..	..
Madras	VWO	4000 m (75 kc/s)	13°–4′N 80°–15′E	289·1 Km.	88°–48′ E of N
Bombay	VUB	357·1 m (840 kc/s)	18°–53′N 72°–48′E	825·2 Km.	37°–30½′ W of N
Colombo	..	428·5 m (700 kc/s)	6°–55′N 79°–53′E	700·2 Km.	158°–44′ E of N
Rugby	GBR	18,750 m (16 kc/s)	52°–23′N 1°–16′W	5049 Km.	39°–10′ W of N
Nauen	DFY	18,130 m (16·545 kc/s)	52°–37′N 12°–49′E	4458 Km.	37°–29′ W of N

APPENDIX II.

The details of the frame aerials are given below :—

No. of Coil	Wave-length range in metres	Shape	Area in sq. m	No. of Turns	Spacing in cm.	Inductance in μH.
1	250–500	Rectangular	1·4	6	1·35	116·6
2	3,000–5,000	Square	3·21	20	1·30	1500
3	15,000–20,000	Square	3·21	50	0·62	7620

APPENDIX III.

The inductance of the coil aerial was calculated from the graph showing the relation between λ^2 and added tuning capacitance for different values of λ. The curves, plotted for the three coils, are shown in Fig. 13. The inductance is given by the formula $L = \frac{\lambda_2^2 - \lambda_1^2}{3 \cdot 55 (C_2 - C_1)}$ in micro-henries, where λ_2 and λ_1 are any two wave-lengths in metres and C_2 and C_1 the corresponding values of the tuning condenser in micromicrofarads.

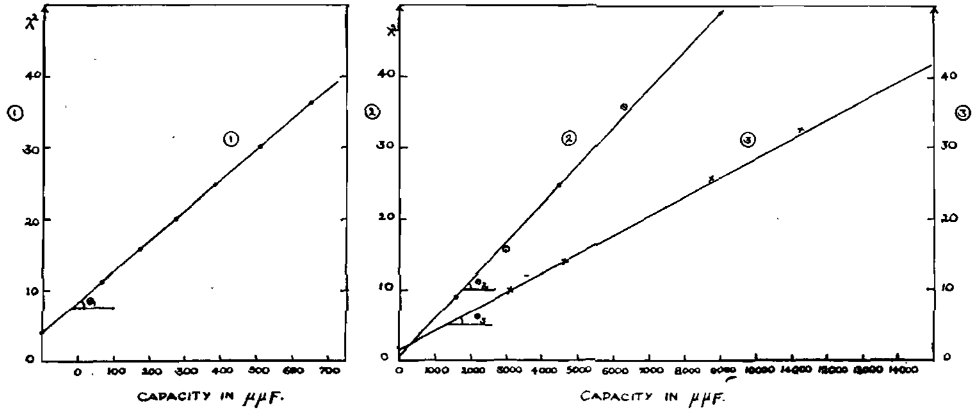

Fig. 13.

$$\text{Tan } \theta = \frac{\lambda_2^2 - \lambda_1^2}{C_2 - C_1} = 3 \cdot 55 \; L_{\mu H.}$$

$$\text{Tan } \theta_1 = \frac{26 \cdot 5 \times 10^4}{640} = 3 \cdot 55 \; L_{\mu H.} \quad (1)$$

$$\therefore \; L = 116 \cdot 6_{\mu H.}$$

$$\text{Tan } \theta_2 = \frac{34 \cdot 1 \times 10^6}{6400} = 3 \cdot 55 \; L_{\mu H.} \quad (2)$$

$$\therefore \; L = 1501_{\mu H.}$$

$$\text{Tan } \theta_3 = \frac{33 \times 10^7}{12200} = 3 \cdot 55 \; L_{\mu H.} \quad (3)$$

$$\therefore \; L = 7620_{\mu H.}$$

APPENDIX IV.

The method of calculating the field intensity is as follows:—
The voltage developed in a coil aerial of area a, and number of turns n, by field intensity F is $\frac{2\pi a n \omega L}{\lambda R} F$, where ω is the angular frequency, λ the wave-length, L the inductance of the coil, and R the effective resistance of the aerial. In the calibrating arrangement let i_1, i_2 be the currents and n_1, n_2 the number of turns in the transformer primary and secondary, respectively. Also let r_1 be the resistance of AB and r_2 the resistance of CD (Fig. 14). C.T. being the current transformer previously mentioned (Dye, *Jour. I.E.E.*, 1925, **63,** 597), we have,

$$i_2 = i_1 \frac{n_1}{n_2}.$$

$$\text{Voltage across AB} = i_2 r_1 = \left(i_1 \frac{n_1}{n_2}\right) r_1.$$

$$\text{Voltage across CD} = \left(i_1 \frac{n_1}{n_2}\right) r_1 \frac{r_2}{r_1} = i_1 \frac{n_1}{n_2} r_2.$$

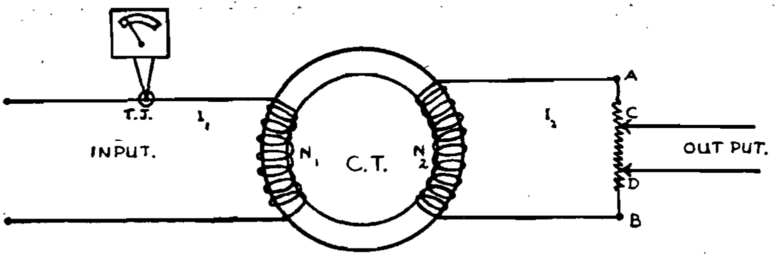

Fig. 14.

The method of measuring the field intensity F consists in **adjusting** r_2 to produce the same deflection as that due to F. Hence

$$V = \frac{2\pi a n \omega L}{\lambda R} F = i_1 \frac{n_1}{n_2} r_2 \quad \cdots \quad \cdots \quad \cdots \quad (1)$$

$$F = \frac{\lambda}{2\pi a n \omega L} \times \frac{n_1}{n_2} \times R\, i_1 r_2 \quad \cdots \quad \cdots \quad \cdots \quad (2)$$

Here F is in volts/cm. when L is in henries, λ in cm., R in ohms, and i in amperes. Expressing F in microvolts/metre the above equation is written as

$$F_{\mu v/m} = \frac{n_1}{n_2} \,.\, \underset{\text{ohms}}{r_2} \,.\, \underset{\text{ohms}}{R.} \; \underset{\text{m.a.}}{i} \left[\frac{\lambda_{\text{m}} \times 10^3}{4\pi^2 a_{\text{sq.m.}} n f L_{\mu\text{H.}}}\right] \quad \cdots \quad \cdots \quad (3)$$

Substituting the corresponding values for λ, a, n, F and L, the above expression for $F_{\mu v/m}$ can be written as follows:—

For observations on

Madras Fort Radio, $F_{\mu v/m} = \frac{n_1}{n_2} r_2 R i_1 \times 14{\cdot}05$

Rugby ,, $\frac{n_1}{n_2} r_2 R i_1 \times 24{\cdot}3$

Nauen ,, $\frac{n_1}{n_2} r_2 R i_1 \times 22{\cdot}72$

Bombay ,, $r_2 R i_1 \times 11{\cdot}05$

Colombo ,, $r_2 R i_1 \times 15{\cdot}92$

r_2 and R are expressed in ohms and i_1 in milliamperes. (*Note :* the calibrating oscillator for Bombay or Colombo does not have a current transformer as can be seen from Fig. 9.)

APPENDIX V.

Measurement of Effective Resistance.

R of the equations in Appendix IV is the effective resistance of the aerial and the amplifier. Equation (1), $\left(i_1 \frac{n_1}{n_2} r_2 = \frac{2\pi a n \omega L}{\lambda R} F\right)$, may be written as $K_1 r_2 = K_2/R$ where K_1 and K_2 are constants depending on the working values of the corresponding terms during experiment. The resistance variation method adopted in the present observations consists in the introduction, while the signal is on, of different additional resistances in the aerial circuit by means of a switch included in the circuit. The deflections in the recorder being noted, the value of R can be calculated from the observations. If R_n and R_m be any two known values of the resistance added to R and the corresponding values of r_2 to produce the same respective deflections be r_n and r_m, we have

$$\frac{K_2}{K_1} = r_2 R = (R + R_n) r_n = (R + R_m) r_m = \text{Constant.}$$

Simplifying, $R = \dfrac{R_m r_m - R_n r_n}{r_n - r_m}$.

The observations were made with a steady signal, obtained from the local oscillator tuned correctly to the station. The deflections on a galvanometer, included in the rectifier circuit, were noted as different resistances were introduced. The double throw switch was next thrown over to the local oscillator and the deflections in the galvanometer were again noted as the resistance r_2 of the potential divider was varied.

A graph, connecting r_2 and galvanometer deflections, was plotted; the resistances r_n, ... , r_m were read corresponding to the deflections obtained as R_n, ... , R_m were introduced in the aerial circuit. Four known resistances were added to R and hence five values for r_2 were read from the graph corresponding to R, $(R + R_n)$, ... , $(R + R_m)$. Taking each pair, ten values were obtained for R and the average of these was taken as the effective resistance.

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STUDIES IN DIELECTRICS.

PART III. THE EFFECT OF SUCCESSIVE DISCHARGES ON THE DIELECTRIC STRENGTH OF LIQUIDS.

By B. S. Ramaswamy, N. V. Narayanaswami and F. N. Mowdawalla.

The dielectric strength of the liquids commonly used as insulating media has been extensively studied all over the world; nevertheless, a test for dielectric strength as carried out normally at present is not a true index of the breakdown strength of the liquid. This is due to the large differences in the values of the breakdown voltage that are obtained in tests carried out under presumably identical conditions. In many cases, particularly in impure oils, the values for two successive tests may differ from each other by as much as 50 per cent. While the differences are smaller in pure oils, they are large enough to render the results of individual tests valueless. It is, however, possible to get a representative value for the B. D. V. of a specimen of oil from the breakdown tests by taking either the arithmetic mean or the most probable value of a number of readings.

Hayden and Eddy (*Journal A. I. E. E.*, 1922, **41**, 491) have passed as many as 500 discharges through samples of transformer oil and benzene in order to ascertain if more uniform values can be obtained after a number of discharges, but found that the differences were of the same order throughout the test. The values differ from the mean by as much as 25 per cent. in transformer oil, 14 per cent. in commercial benzene, 12 per cent. in pure benzene and 4 per cent. in air. They ascribe the large differences in transformer oil to the complexity of its chemical structure. Rebhan (*E.T.Z.*, 1932, **53**, 556) has studied the application of the statistical method to the determination of the B. D. V. of transformer oil by applying the Gauss's correction curve. In the case of pure oil the difference between the arithmetic mean and the most probable value estimated by this method for 30 successive readings was found to be 4 per cent. His results show that the difference between the arithmetic mean and the most probable value diminishes as the number of readings increases. Hence the arithmetic mean of a large number of values can be taken to represent the breakdown strength of a sample without any great error.

However, the passage of a large number of discharges through a liquid alters its composition and thus introduces a fresh complication. Due to the high temperature attained in the path of the discharge, a small quantity of the liquid evaporates while another small quantity is decomposed. Thus impurities are introduced into the liquid in the shape of the oil vapour and the products of decomposition, namely, carbon and gases. Further, with repeated discharges metallic impurities are also introduced into the oil from the electrodes. The experiments of Gemant (*Zeits. f. Physik*, 1925, **33**, 789), Koppelmann (*E.T.Z.*, 1930, **51**, 1457) and others have shown that in moist liquids, on the application of an electric stress, moisture is drawn into the test gap in the form of fine globules. At each discharge a portion of the moisture evaporates and the oil becomes drier.

The experiments of Hayden and Eddy (*loc. cit.*) and Koppelmann (*loc. cit.*) have not revealed the effect of the progressively changing composition of the oil with successive discharges. The present experiments carried out with 3 000 successive discharges in each set of tests clearly show a definite drift in the mean value of the B. D. V. due to the combined effects of increasing impurities and the progressive drying of the oil.

The present investigation was originally undertaken with a view to standardising the preparation of oil for various studies of its dielectric behaviour. As a preliminary, it was decided to investigate the conditions causing the divergences in the values of the breakdown voltage. It was in the course of this investigation that the drift was first observed and carefully studied.

EXPERIMENTAL.

High Voltage Supply.—The scheme of connections for the test circuit is shown in fig. 1. A 50 volt, 25 cycle supply was connected

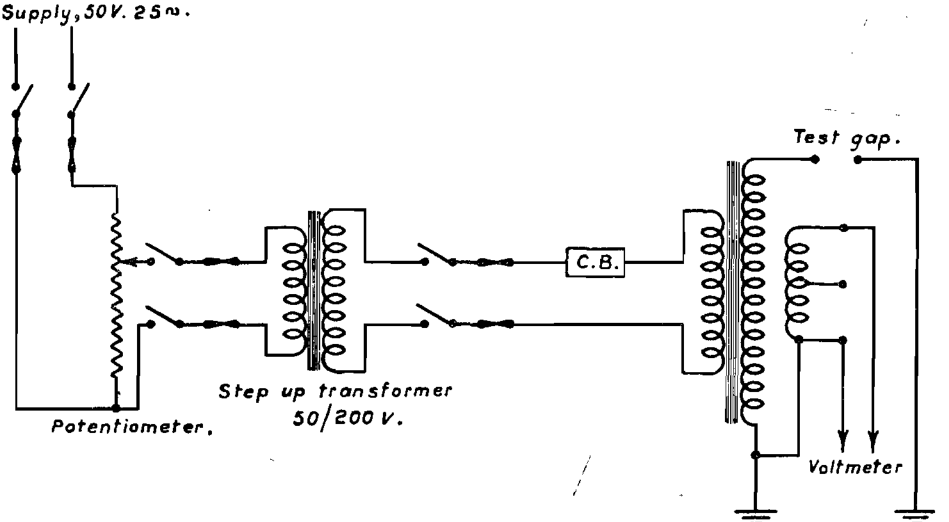

Fig. 1.

Diagram of Connections.

across a potentiometer, the variable voltage output from which was supplied to a step-up transformer. The secondary of this transformer supplied the high voltage testing transformer having a ratio of 220/115 000 volts. The secondary voltage of the testing transformer was measured by means of a low tension voltmeter connected to a tertiary winding provided in the transformer.

In order to obtain comparable results the test voltage was increased at a constant rate of about 12 kV per second throughout the tests. This high rate of increase was adopted in order to minimise the time for each set of 3 000 discharges which required about four hours.

Test cells.—Two rectangular glass vessels were used in the experiments. The larger one had a capacity of 1 000 c.c. of the test liquid while the capacity of the smaller one was 450 c.c. The two cells of different capacities were required for the purpose of investigating the effect of the volume of the liquid on the drift of the mean B. D. V.

The electrodes consisted of $\frac{1}{2}''$ diameter brass spheres complying with British Standard Specification No. 148 of 1927 and were supported as shown in fig. 2. The gap was adjustable and was maintained at 0·15″ throughout the tests.

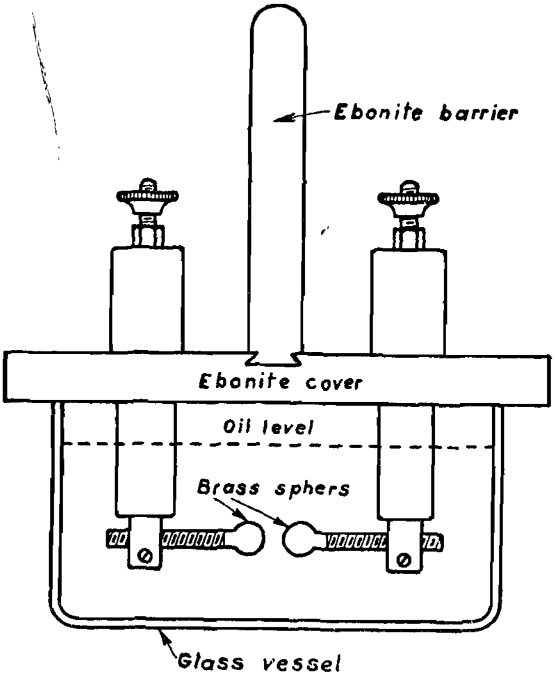

Fig. 2.

Liquids tested.—The *transformer oil* used in the investigation was Transil No. 10 c supplied by the International General Electric Company of America. It was pale yellow in colour and had the following constants :

Specific Gravity	..	0·885
Flash Point	..	295°F.
Redwood Viscosity	..	62″ at 25°C.

The oil from stock was purified by passing it twice through well-dried filter paper in a filter press after which it was stored in clean dry glass bottles.

Moist oil required for the experiments was prepared by blowing moist air through the purified oil. For this purpose air was forced through a bottle of water by means of a blower. It was next allowed to pass through an empty bottle which served as a water trap and then bubbled through the test sample. The arrangement is shown in fig. 3.

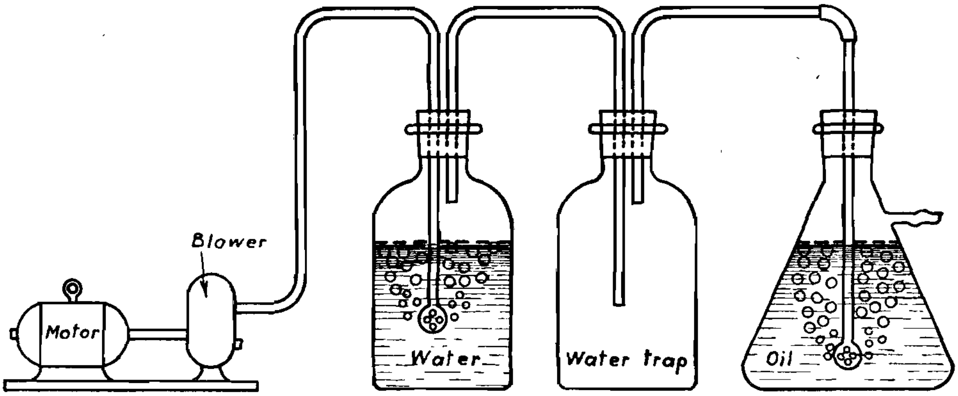

Fig. 3.

Arrangement for Preparing Samples of Moist Oil.

The moisture content of the specimen depended upon the length of time the moist air was blown through it.

Benzene was also experimented with. In this case it was found sufficient to pass the samples through a number of dry filter papers for drying. Moist benzene was prepared by shaking up pure benzene with small known quantities of distilled water. The moisture content was therefore known accurately in this case.

Method of testing.—Extreme precautions were taken to prevent fibres and other impurities from getting into the test sample. For this purpose the test cell was first scrupulously cleaned and rinsed two or three times with pure oil, after which it was filled with oil. The electrodes which were carefully cleaned previously were then immersed into it and the voltage applied. The voltage, equal to the maximum that the oil could withstand without breaking down, was maintained for half an hour. It was then switched off and, after rinsing the electrodes, the oil was rejected. This process was repeated two or three times until all the fibres from the electrodes and the test cell were removed.

The test sample was then introduced into the vessel and the test voltage applied and increased at the prescribed rate until the liquid broke down. The voltage at which breakdown occurred was noted each time. From the readings thus obtained, the averages of every hundred shots, starting from the first, were calculated.

RESULTS.

Tests with oil.—Fig. 4 represents the results of tests carried out in the larger vessel with 1 000 c.c. of oil. Curve 1 shows the effect of successive discharges in the case of pure dry oil. Curves 2 to 5 show the results obtained with the same oil having progressively increasing moisture content. The values of B. D. V. plotted in these graphs are the averages of 100 readings.

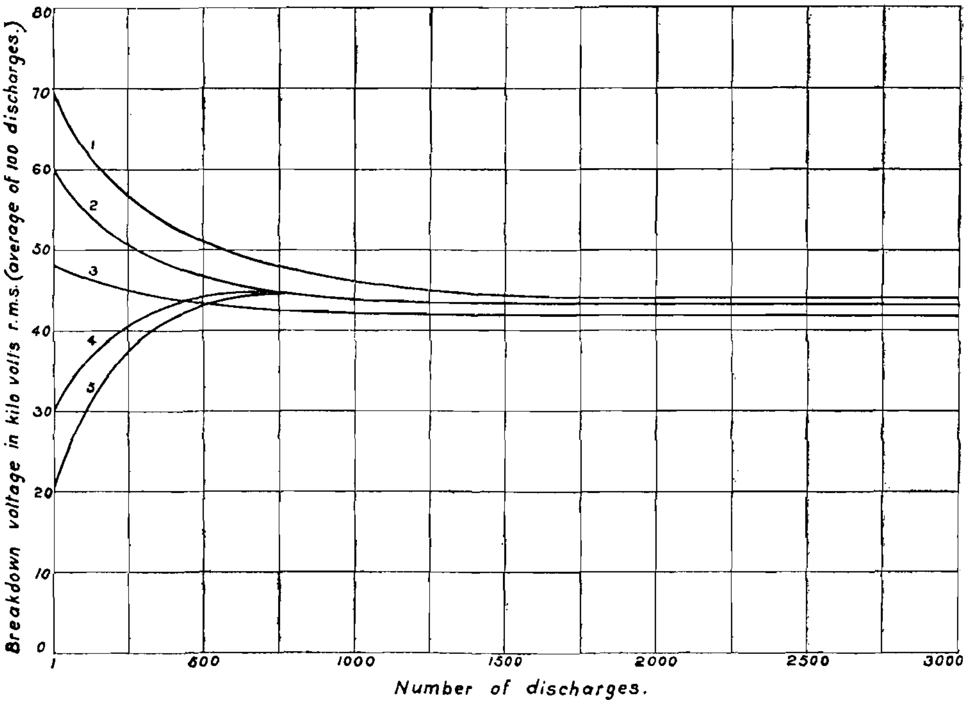

Fig. 4.

Successive Discharges in 1 000 c.c. of Transformer Oil.

With increasing moisture content, the initial B. D. V. drops from 70 kV in the case of pure oil to 20 kV in the case of saturated oil. In the case of dry oil with an initial B. D. V. of 70 kV (curve 1) the effect of successive discharges is to lower the value of the B. D. V. which decreases very rapidly at first, but less and less rapidly as the number of discharges increase, until it reaches a steady value of about 44 kV after about 1 500 discharges. With slightly moist oil having an initial B. D. V. of 60 kV (curve 2) the rate of decrease is less rapid and the final steady value of 43 kV is reached after about 1 000 discharges. With moist oil having an initial B. D. V. of 48 kV, the fall is very small but the steady value of 42 kV is again reached after about 1 000 discharges. With very moist oils (curves 4 and 5) there is an initial rise, instead of a fall, of B. D. V. The rise is more rapid in the case of the moister sample (curve 5), but in both cases the final steady value of 43 kV is attained after about 1 000 discharges. Thus, allowing for errors of observation, we obtain the remarkable result that in all cases the B. D. V. settles down to a final steady value of about 43 kV after about 1 000 discharges. It may be concluded from these graphs that in a sample with an initial B. D. V. of about 43 kV, there would be little change in B. D. V. at all points.

The above results can be explained as follows: As mentioned before, the effect of each discharge is (1) to produce a small quantity of carbon and other products of decomposition and (2) to remove a small quantity of moisture from the oil. These two factors affect the B. D. V. in opposite directions. The addition of carbon tends to lower the B. D. V. while the removal of moisture tends to increase it. It was found by a separate experiment that the total amount of carbon produced by each of the three thousand successive discharges was the same. It may therefore be assumed that the same quantity of carbon is produced by each discharge in the case of each sample. On the other hand the amount of moisture removed at each discharge may be regarded as varying with the samples, depending upon their moisture content. Thus it can be assumed that in moist oil a larger quantity of moisture would be removed at each discharge than in a drier sample.

V. may

With increasing moisture content, the initial B. D. V. drops from 70 kV in the case of pure oil to 20 kV in the case of saturated oil. In the case of dry oil with an initial B. D. V. of 70 kV (curve 1) the effect of successive discharges is to lower the value of the B. D. V. which decreases very rapidly at first, but less and less rapidly as the number of discharges increase, until it reaches a steady value of about 44 kV after about 1 500 discharges. With slightly moist oil having an initial B. D. V. of 60 kV (curve 2) the rate of decrease is less rapid and the final steady value of 43 kV is reached after about 1 000 discharges. With moist oil having an initial B. D. V. of 48 kV, the fall is very small but the steady value of 42 kV is again reached after about 1 000 discharges. With very moist oils (curves 4 and 5) there is an initial rise, instead of a fall, of B. D. V. The rise is more rapid in the case of the moister sample (curve 5), but in both cases the final steady value of 43 kV is attained after about 1 000 discharges. Thus, allowing for errors of observation, we obtain the remarkable result that in all cases the B. D. V. settles down to a final steady value of about *43 kV after about 1 000 discharges.* It may be concluded from these graphs that in a sample with an initial B. D. V. of about, 43 kV, there would be little change in B. D. V. at all points.

The above results can be explained as follows: As mentioned before, the effect of each discharge is (1) to produce a small quantity of carbon and other products of decomposition and (2) to remove a small quantity of moisture from the oil. These two factors affect the B. D. V. in opposite directions. The addition of carbon tends to lower the B. D. V. while the removal of moisture tends to increase it. It was found by a separate experiment that the total amount of carbon produced by each of the three thousand successive discharges was the same. It may therefore be assumed that the same quantity of carbon is produced by each discharge in the case of each sample. On the other hand the amount of moisture removed at each discharge may be regarded as varying with the samples, depending upon their moisture content. Thus it can be assumed that in moist oil a larger quantity of moisture would be removed at each discharge than in a drier sample.

In the case of dry oil (curve 1) the entire change of B. D. V. may be regarded as being due to the accumulation of carbon and the B. D. V. therefore drops. The curve is similar to that in fig. 5, obtained for pure oil by adding increasing doses of carbon previously prepared by passing discharges through a quantity of oil. It can be seen from fig. 5 that the effect of the addition of carbon is to lower the B. D. V. The fall is very rapid at first but becomes less and less rapid as the carbon content increases until finally a steady value is reached and further addition of carbon produces no effect on the B. D. V. In the case of the samples containing small quantities of moisture (curves 2 and 3), there is the further effect of the removal of moisture *at each discharge, which tends to raise the B. D. V. However, the effect* of accumulation of carbon predominates and the net result is that the B. D. V. falls, the decrease being more rapid in the case of the drier sample but not as rapid as in the case of the dry sample (curve 1). In very moist oils (curves 4 and 5) the effect of the removal of moisture is predominant and the B. D. V. rises, the increase being more rapid in the case of the moister sample. In all cases so long as the carbon content is small, the B. D. V. is determined jointly by the moisture and carbon content but, after about 1 000 discharges, when a large amount of carbon has accumulated and the moisture content has become very small even in the wettest sample, the B. D. V. is determined solely by the carbon content and all curves become coincident.

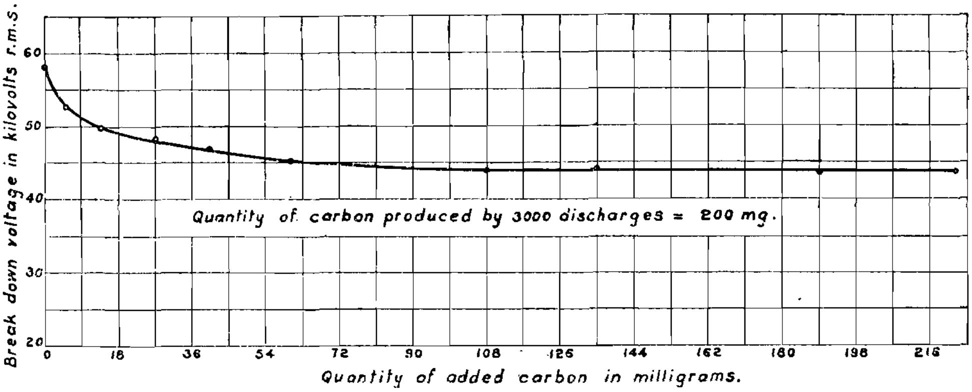

Fig. 5.

Effect of added Carbon on the B.D.V. of Transformer Oil.
(Quantity of Oil, 450 c.c.)

Effect of size of test cell.—Fig. 6 shows the results of similar tests carried out in the smaller vessel with 450 c.c. of oil. The curves are similar to those in fig. 4 but, for corresponding samples, the rate of change of B. D. V. is greater and the final steady value is reached in all cases after about 500 discharges instead of 1 000 discharges. This can be explained as follows:

Quantitative tests have shown that 0·2 g. of carbon was produced in both large and small vessels as a result of 3 000 discharges in each case. The quantity of carbon produced at each discharge may therefore be regarded as being the same in each case. Similarly, it may be assumed that under similar conditions of moisture content the amount of moisture removed at each discharge is the same in the case of tests carried out in both the vessels. Consequently, starting with similar samples of oil, the increase of concentration of carbon and the decrease of concentration of moisture in the smaller vessel would be more rapid than in the larger vessel and the B. D. V. would change more rapidly.

This is borne out by the result that the final steady values in the two sets of tests are reached after 500 and 1 000 discharges, respectively, since the ratio of these figures is approximately the same as the ratio of the capacities of the two vessels.

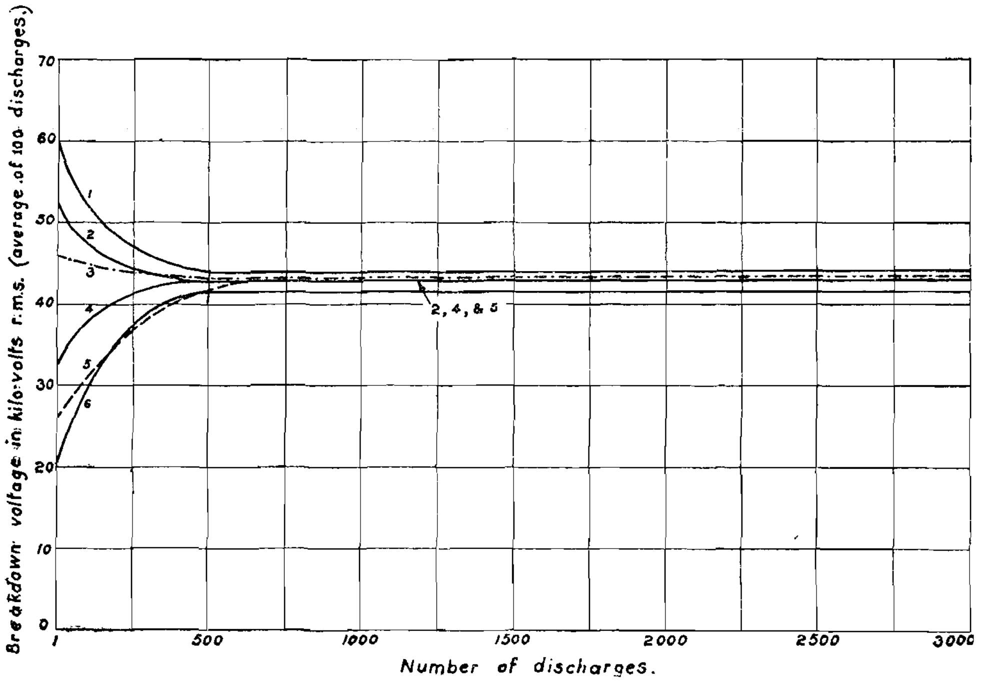

Fig. 6.

Successive Discharges in 450 c.c. of Transformer Oil.

Tests with benzene.—Similar tests were also carried out in the smaller test vessel with 450 c.c. of (*a*) dry benzene and (*b*) benzene containing respectively, 0·067, 0·134, 0·20, and 0·267 c.c. of water. The results given in fig. 7 show the same characteristics as those obtained with oil. The curves clearly indicate the two-fold effect, namely, the lowering of B. D V. due to the accumulation of carbon and the increase due to the expulsion of moisture. In the case of the dry sample there is an initial fall and in all the moist samples there is an initial rise. The final steady value is reached in all cases after 1 000 discharges. There is, however, a noteworthy difference. In the case of moist samples of benzene, each curve shows a maximum value of B. D. V. These maxima can be explained as follows. Initially, the effect of expulsion of moisture is more important than that of the accumulation of carbon with the result that the B. D. V. increases. With increasing number of discharges the improvement of B. D. V. due to expulsion of moisture becomes less and less rapid until (in the case of curve 5) this effect becomes exactly neutralized by the effect of accumulation of carbon after about 400 shots beyond which the effect of the increasing carbon content becomes more predominant and the curve drops again. Considering the other curves the maximum value is reached after a progressively smaller number of shots with benzene of increasing dryness. This is because with drier benzene the effect of removal of moisture becomes less and less important as compared with that of accumulation of carbon. It will also be noticed that the portion of the curves before the maximum value is reached is steepest for curve 5 and progressively less so for curves 4, 3 and 2, respectively. It may be presumed that similar maxima would be exhibited by the curves for oil if at each discharge the removal of moisture were more rapid or the production of carbon smaller.

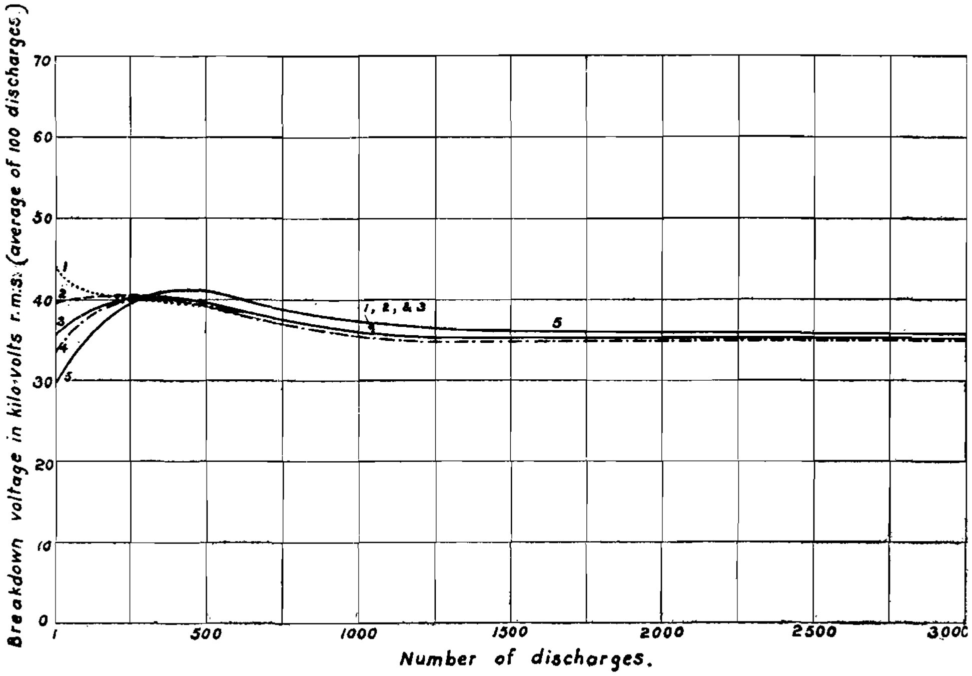

Fig. 7.

Successive Discharges in 450 c.c. of Benzene.

Application to Oil Circuit-Breakers.—The above results have an important bearing on the insulating value of oil used in circuit-breakers. The minimum B. D. V. of oil used in transformers and circuit-breakers as specified in British Standard Specification No. 148 of 1927 under standard gap conditions is 22 kV. This corresponds to the very moist oils used in the above tests and in the case of such oils the effect of successive discharges is to improve the B. D. V. instead of lowering it, as indicated by the results shown in figs. 4 and 6. It would thus appear that the carbon produced by the discharges has no deleterious effect on the insulating strength of moist oils, and from the point of view of the B. D. V. of oil it would not be necessary to filter out the carbon produced by the discharges due to the automatic opening of the circuit-breaker under fault conditions. In the case of dry oil, although the accumulation of carbon does lower their B. D. V. the minimum value attained on account of this cause is not less than 43 kV and as this value is well above the specified minimum no difficulty can arise from this source.

CONCLUSIONS.

The B. D. V. of comparatively dry specimens of transformer oil having B. D. V. exceeding 43 kV (BSS test gap), when subjected to successive discharges, decreases until it reaches about 43 kV after about 1 000 discharges after which it remains constant when subjected to further discharges. The B. D. V. of moist samples of transformer oil having B. D. V. below 43 kV, when subjected to successive discharges, increases until it reaches the steady value after the same number of discharges. This is explained by the joint action of the accumulation of carbon and the removal of moisture. With smaller test cells the same result is obtained with a smaller number of discharges. The B. D. V. of benzene when subjected to successive discharges similarly decreases to a final steady value of about 35 kV. In this case, however, maximum values are obtained which are explained in the paper. The bearing of these results on the operation of oil circuit-breakers is discussed and it is shown that in the case of moist oil the effect of the discharge when the circuit-breaker opens under fault conditions is to improve rather than lower its B. D. V.

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STUDIES IN DIELECTRICS.

PART IV. THE EFFECT OF IMPURITIES ON THE BREAKDOWN VOLTAGE OF TRANSFORMER OIL.

By B. S. Ramaswamy, N. V. Narayanaswami and
F. N. Mowdawalla.

Insulating oils used in transformers are liable to contamination by impurities like cotton and pressboard fibres and insulating varnishes absorbed from the transformer. Moreover, sludge is formed in the oil due to oxidation. All these impurities together with the moisture present in the oil considerably influence its dielectric strength and, when present in large quantities, may render it unfit for use.

Hirobe (*Tokyo Electrotechnical Lab. Report*, No. 25, Section iii) was the first to show that small fibres of cotton and other insulating materials in moist oils considerably lower their breakdown strength. Mclaughlin (*Electrician*, 1921, **86**, 325) reports having observed a sudden increase in the conductivity of oil containing fibres and dust particles. He concludes from the consideration of conductivity that moist fibres should greatly reduce the dielectric strength of oil. The actual formation of liquid and fibre bridges has been observed by many investigators. Armstrong (*Electrical World*, 1913, **62,** 1322) attempted the study of the effect of rubber on the B. D. V. of transformer oil. After keeping a small piece of rubber in contact with oil for several hours, he noted a large drop in the dielectric strength of oil. His result is only qualitative and has not been verified by any other investigator.

The effects of oxidation of transformer oil have been studied by Ornstein (*Archiv. f. Elektrot*, 1933, **27**, 489) and others from a purely chemical point of view. Elsa Pechmann (*Archiv. f. Elektrot*, 1932, **26,** 46) has investigated the effect of heating, in the presence of oxygen, nitrogen and lac-impregnating material on the colour, acid number, saponification number and tar number of insulating oil. The results show that the worst effects are produced by the lac-impregnating material. This work is purely chemical in character and does not concern itself with dielectric properties at the various stages of the reactions. F. M. Clark (*Journal Frank. Inst.*, 1933, **215,** 39 and 1933, **216,** 429) has investigated the action of dissolved gases on the dielectric strength of transformer oil. He comes to the conclusion that a test of the dielectric strength as carried out at present is really a test of the dissolved gas or gasifiable matter contained in the oil and hence the B. D. V. can be modified by modifying its gas solubility

A systematic investigation of the behaviour of transformer oil con-
ning impurities such as cotton and pressboard fibre, moisture and rbon has been made by the British Electrical and Allied Industries search Association (*Journal I.E.E.*, 1929, **67,** 750). This estigation has shown that while any one of these impurities by itself s a small effect on the B. D. V. of dry transformer oil, fibres in mbination with moisture can produce a very great lowering of the electric strength. In the presence of moisture carbon appears to have e least and cotton fibre the greatest effect. 500 mg. of carbon with ·92 c.c. of water in 10 000 c.c. of oil reduces the B. D. V. from 100 to 0 kV while 2 mg. of cotton fibre with 1·21 c.c. of water in 10 000 c.c. f oil lowers it to 20 kV.

The above report, however, does not cover all the impurities in ansformer oil. In addition to fibres, carbon and moisture, other npurities likely to be present are sludge, insulating varnishes and waxes sed for transformer coils. These varnishes and waxes, though good nsulators themselves, might still reduce the dielectric strength of oil. study of their effect on the breakdown voltage of insulating oil ppears, therefore, to be of great interest and importance. The present nvestigation deals with the effect of traces of alcohol, shellac, paraffin ax and sludge on the B. D. V. of transformer oil. The effect of arbon has already been studied and the results are given in Part III. n addition to the study of the effect of these impurities on the dielectric rength of oil, the effect of a large number of successive discharges rough oil containing these impurities has also been investigated.

EXPERIMENTAL.

High Voltage Supply.—The high voltage required for the urposes of the tests was obtained as described in Part III and the iagram of connections is shown in fig. 1 in Part III.

Test cell.—The test cell and the electrodes used for this investigation were similar to those described in Part III. The cell was similar to the smaller cell used for the experiments with successive discharges and had a capacity of 450 c.c. of oil.

Method of testing.—The preparation of pure, dry oil and the method of cleaning the cell and the electrodes to make them fibre-free have been described in the previous part.

Preparation of test samples.—The test samples were prepared by adding requisite quantities of the impurities, prepared as follows, to 450 c.c. of pure transformer oil.

Paraffin wax.—1 gram of pure paraffin wax was added to 25 c.c. of pure dry transformer oil, and the mixture was warmed and well shaken. The paraffin dissolved and the solution was used after cooling as required.

Alcohol.—1 c.c. of alcohol was added to 25 c.c. of pure dry transformer oil and shaken well to form an intimate mixture. Small quantities of this mixture were added, as required, to the test sample of oil which was then well stirred with a clean glass rod.

Shellac.—An unbleached variety of shellac was first powdered so as to pass through a 200-mesh sieve and made into a suspension in oil; this suspension was added to the test sample as required. For another series of tests the shellac was first dissolved in alcohol. On spreading the solution on a glass plate and allowing the alcohol to evaporate, thin films of shellac were obtained. They were scraped out and powdered so as to pass through a 200-mesh sieve. A suspension of this powder in a small quantity of dry oil was prepared as before and added to the test sample as required.

Sludge.—With the object of determining the effect of sludge formed in oil in the presence of copper, the method described in the British Standard Specification No. 148 of 1927 for sludging tests of insulating oils was used with a slight modification for the preparation of sludge. The only difference was that a bigger flask containing a larger quantity of oil was used and the quantity of sludge formed after 45 hours was found to be 0·75 g. in 100 c.c. of oil. This sludged oil had a B. D. V. of 38 kV while the pure oil before sludging had a B. D. V. of 70 k V.

Mixture of impurities.—In order to study the combined effect of some of the impurities, when present together, on the B. D. V. of oil a mixture was prepared as follows: 1·5 g. of paraffin wax was dissolved in 50 c.c. of sludged oil and 0·5 g. of shellac powder was added to this mixture. This mixture was added to the test sample of transformer oil as required.

Estimation of the breakdown voltage.—The estimation of the breakdown voltage is rendered difficult owing to the great divergences in the values obtained under identical test conditions. Hence, in such an investigation, the method of determining the breakdown voltage is very important. Very few of the previous investigators seem to be clear on this point. In order to obtain consistent results the average of ten successive breakdown readings each time was taken to represent the B. D. V. of the oil. The effect of each impurity was studied by adding it successively in small doses to the same sample of oil, the B. D. V. at each stage being measured by ten successive breakdown tests as referred to above.

In this method of conducting the tests, a small amount of carbon is introduced into the oil at each discharge, which may affect the B. D. V.

As it is not possible to eliminate this, it was necessary to minimise the number of discharges without at the same time making it too small for consistent results. In order to ascertain the extent to which the B. D. V. was affected by this carbon, experiments were conducted with varying doses of the impurity thereby altering the total number of discharges passed in each set of readings. It will be seen from the graphs that the influence of carbon as compared to that of the impurity is negligible.

RESULTS.

Effect of alcohol.—The results obtained with alcohol are shown in fig. 1. Curves 1, 2, 3 and 4 represent the result of adding 1 c.c. of alcohol to 450 c.c. of pure dry oil in doses of 0·04, 0·08, 0·16 and 0·24 c.c., respectively. The curves drop rapidly at first, but less and less rapidly with further additions until a practically steady value is reached when 0·4 c.c. has been added and the addition of further

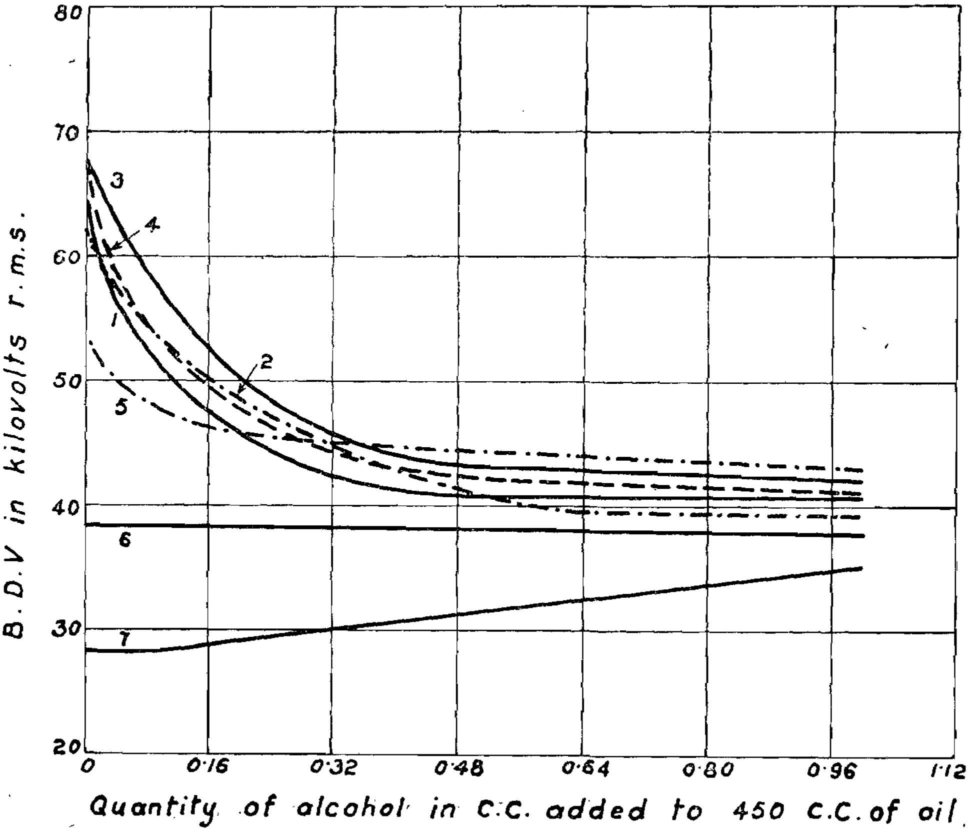

Fig. 1.

Effect of Alcohol on the B.D.V. of Transformer Oil.

quantities has little effect. In all cases the final steady value is about 40 kV. Allowing for the divergences in the graphs due probably to slight differences in the initial moisture content of the four test samples, all the curves are substantially the same, indicating that the effect of the products of decomposition produced by the discharges is negligible in comparison with that of alcohol.

Curves 5, 6 and 7 represent the effect of the addition of alcohol in doses of 0·08 c.c. to oils with different moisture content. In a slightly moist sample (curve 5) the drop is smaller than in the dry samples. This indicates that the effect of alcohol is partly neutralised by the effect of removal of moisture due to the discharges. In a moister sample having an initial B. D. V. of 38 kV, the curve remains level, indicating that the two effects are exactly balanced. In the wettest sample having an initial B. D. V. of 28 kV the curve rises instead of falling. This is because in this case the effect of the removal of moisture predominates.

In all these cases the final steady value does not appear to have been reached when 1 c.c. of alcohol has been added. In curves 5 and 7 this is apparent. In order to bring this out more clearly in the case of the dry sample, the effect of the addition of a larger quantity of alcohol is represented in fig. 2 which shows that the final steady value of 37·5 kV is not reached before nearly 2 c.c. have been added.

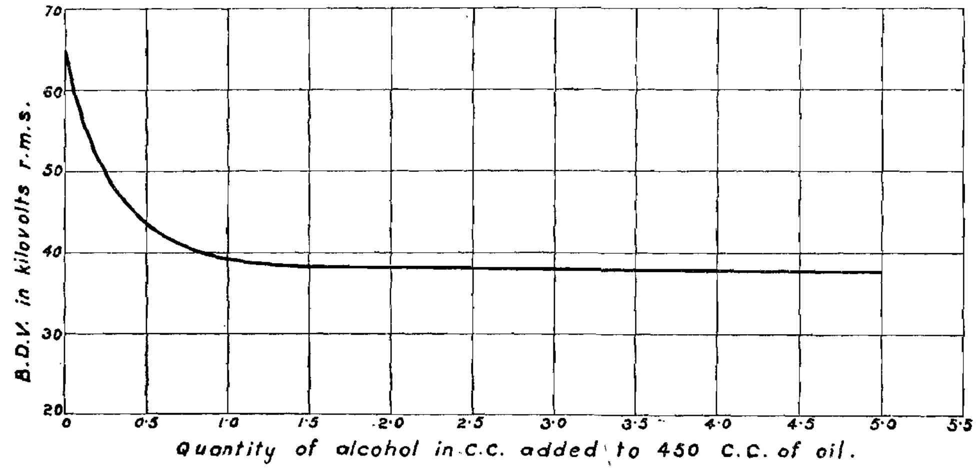

Fig. 2.

Effect of Alcohol (Large Quantity) on the B.D.V. of Transformer Oil.

Fig. 3 shows the effect of successive discharges on dry oil containing 1 c.c. of alcohol. The low initial B. D. V. (40 kV) is due to the presence of alcohol. This steadily rises with successive discharges, due probably to the removal of alcohol, until a final steady value of 44·5 kV is reached after about 1 000 discharges.

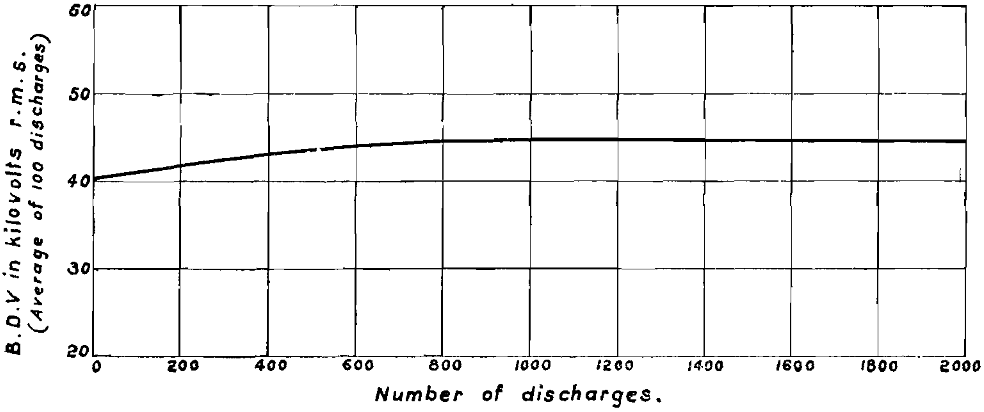

Fig. 3.

Successive Discharges in 450 c.c. of Transformer Oil containing 1 c.c. of Alcohol.

Effect of shellac—(*i*) *Unbleached shellac.*—Fig. 4 represents the effect of unbleached shellac when added to oil. Curves 1, 2, 3 and 4 show the effect of adding it to dry oil in doses of 0·025, 0·05, 0·075 and 0·1 g., respectively. The nature of the curves is similar to that obtained with alcohol, but the final steady value does not seem to have been reached when 0·50 g. has been added.

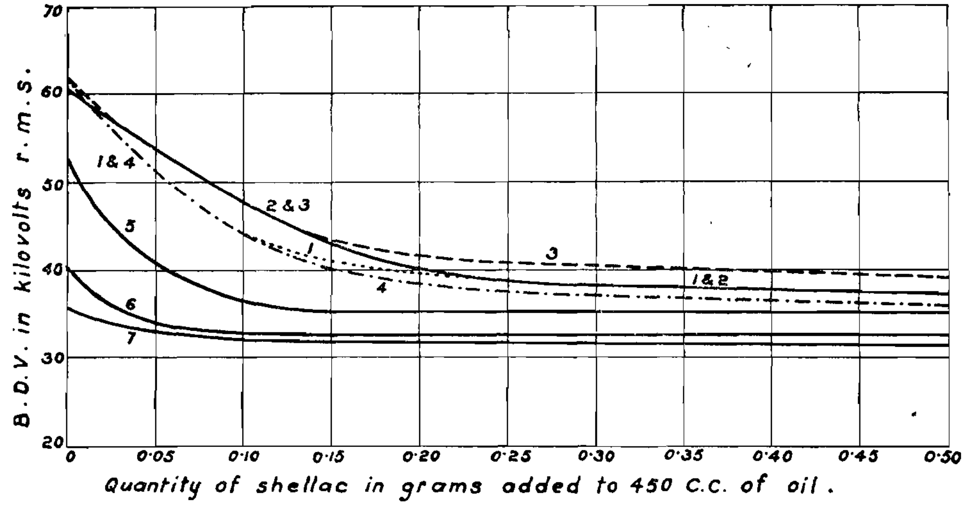

Fig. 4.

Effect of Unbleached Shellac on the B.D.V. of Transformer Oil.

Curves 5, 6 and 7 show results obtained by adding shellac in doses of 0·05 g. to oils of varying moisture content. In all cases there is an initial drop which indicates that the lowering of B. D. V.

produced by the addition of shellac is greater than the effect of the drying of oil due to the discharges. However, the initial drop is smaller the moister the oil, and it may be presumed that with oil having an initial B. D. V. below 31 kV there would be a rise instead of a drop.

The results obtained by subjecting samples of oil with varying moisture content to successive discharges after adding 0·5 g. of shellac are shown in fig. 5 which shows that in all cases the B. D. V. rises and finally reaches a steady value of about 39 kV. This is probably due to the drying effect of the discharges.

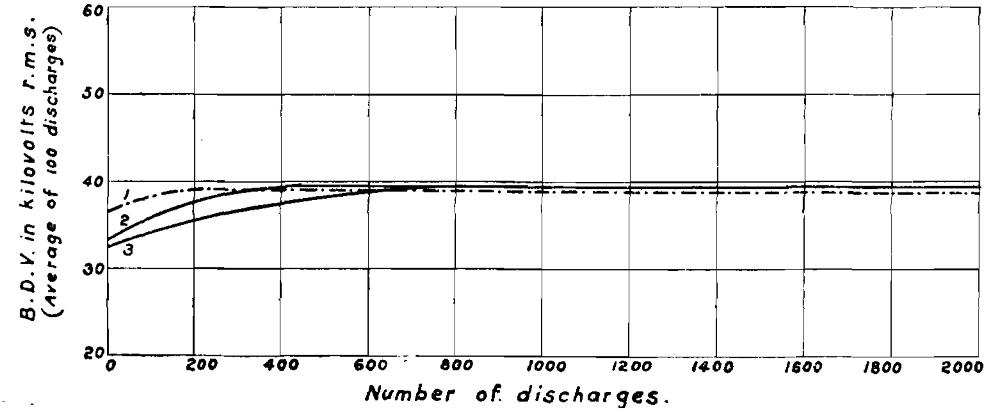

Fig. 5.

Successive Discharges in 450 c.c. of Transformer Oil containing 0·5 grams of Shellac.

(*ii*) *Shellac purified by solution in alcohol and subsequent drying.*—The results obtained by adding shellac, prepared from solution in alcohol and subsequent drying, in doses of 0·025, 0·05, 0·075 and 0·1 g. are shown in fig. 6 and are substantially the same as for unbleached shellac shown in fig. 4. This indicates that the impurities in unbleached shellac have little, if any, effect on the B. D. V. of oil.

Effect of paraffin wax.—Fig. 7 shows the effect of paraffin wax when added to dry oil in doses of 0·05, 0·1, 0·15, 0·2, 0·25 and 0·3 g., respectively. There is nothing noteworthy about these curves which are similar to those in figs. 1 and 4. The effect of the wax on moist oil, shown in fig. 8, is more interesting. Curves 1 and 2 were obtained with 0·1 g. doses and curve 3 with 0·05 g. doses of wax. All these curves pass through a minimum before reaching the final steady value. This can be explained by assuming that initially the effect of addition of wax is greater than the drying effect produced by the discharges; at the point corresponding to the minimum value the two effects are equal and thereafter the effect of drying predominates.

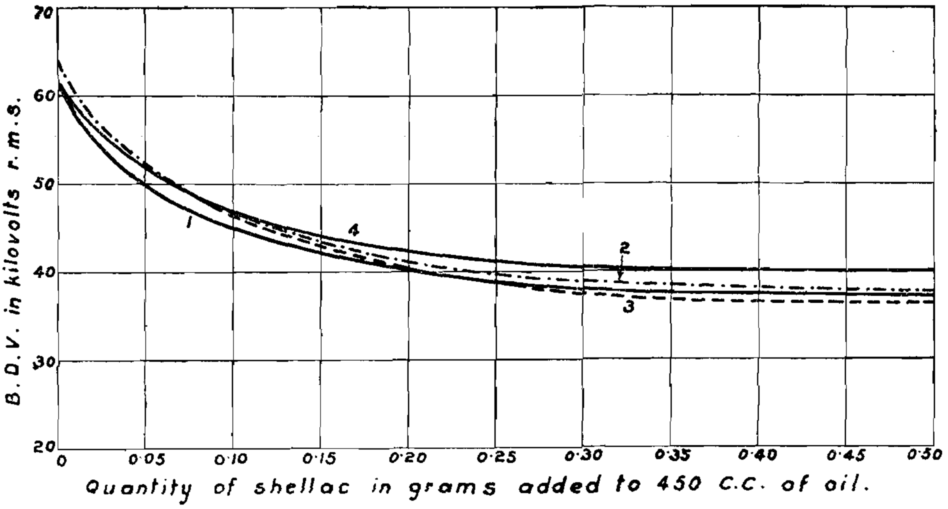

Fig. 6.

Effect of Shellac (dissolved in Alcohol and dried) on the B.D.V. of Transformer Oil.

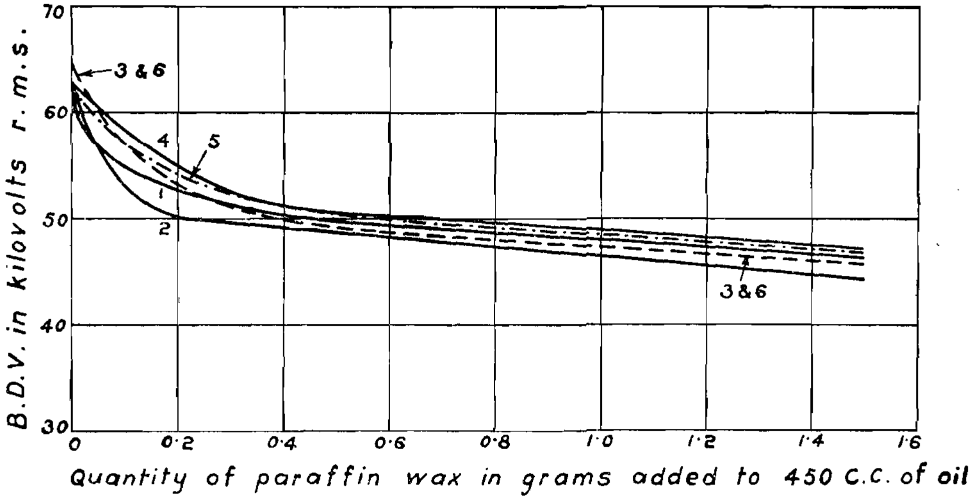

Fig. 7.

Effect of Paraffin Wax on the B.D.V. of Transformer Oil.

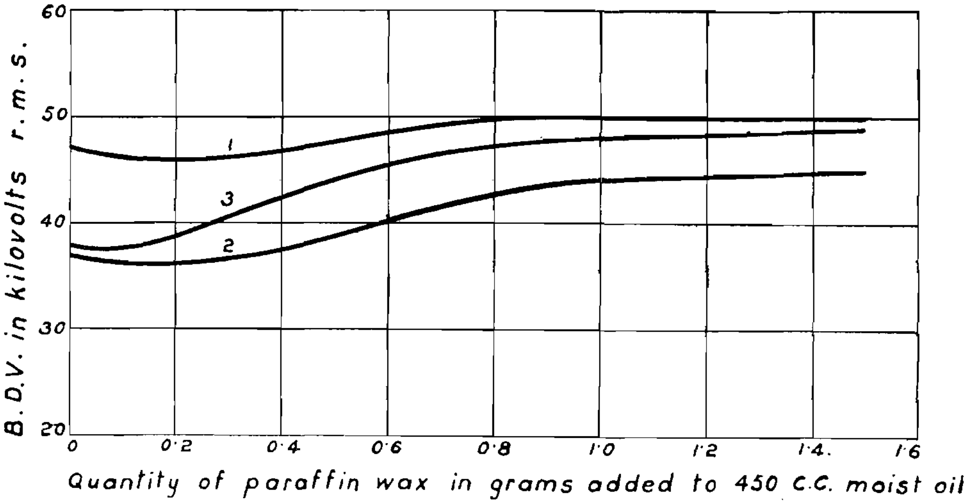

Fig. 8.

Effect of Paraffin Wax on the B.D.V. of Moist Transformer Oil.

This is borne out by curve 3 in which the number of discharges is doubled due to the smaller dosage. Consequently the minimum point is reached earlier and the curve rises steeper.

The effect of successive discharges on dry and moist oil is shown in fig. 9. But for the initial lowering of B. D. V. the addition of paraffin wax does not seem to alter the B. D. V. of oil.

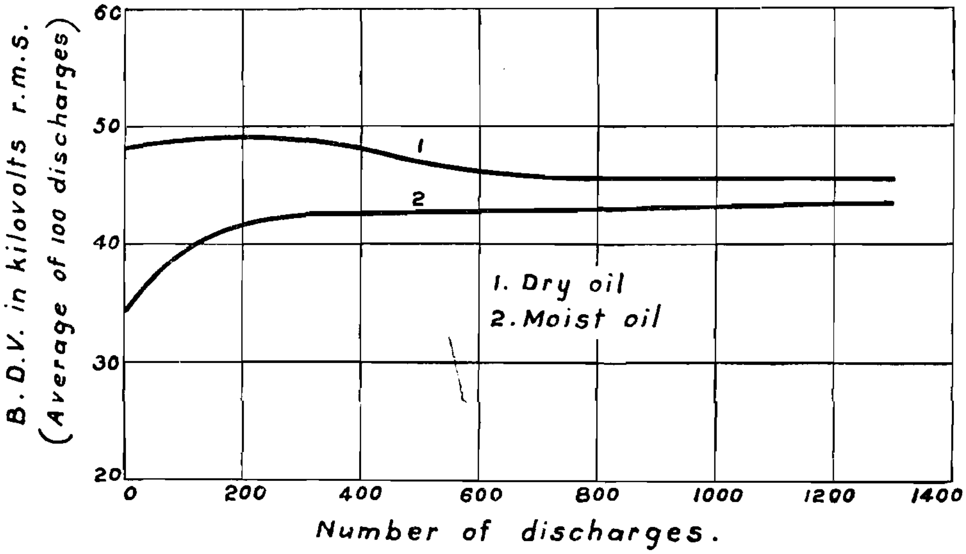

Fig. 9.

Successive Discharges in 450 c.c. of Transformer Oil containing 1·5 grams of Paraffin Wax.

Effect of sludge.—The curves in fig. 10 representing the effect of sludge are similar to the curves for other impurities. Curves 1, 2 and 3 correspond to the addition of 1, 2 and 5 c.c. doses respectively, to dry oil, while curve 4 is for moist oil. In dry oil considerable further addition of sludge would be necessary to bring it to its final steady value of B. D. V. This value cannot fall below 38 kV which is the B. D. V. of the sludged oil obtained as explained before. In moist oil a constant value is obtained, as in the case of shellac, with a very small quantity of sludge.

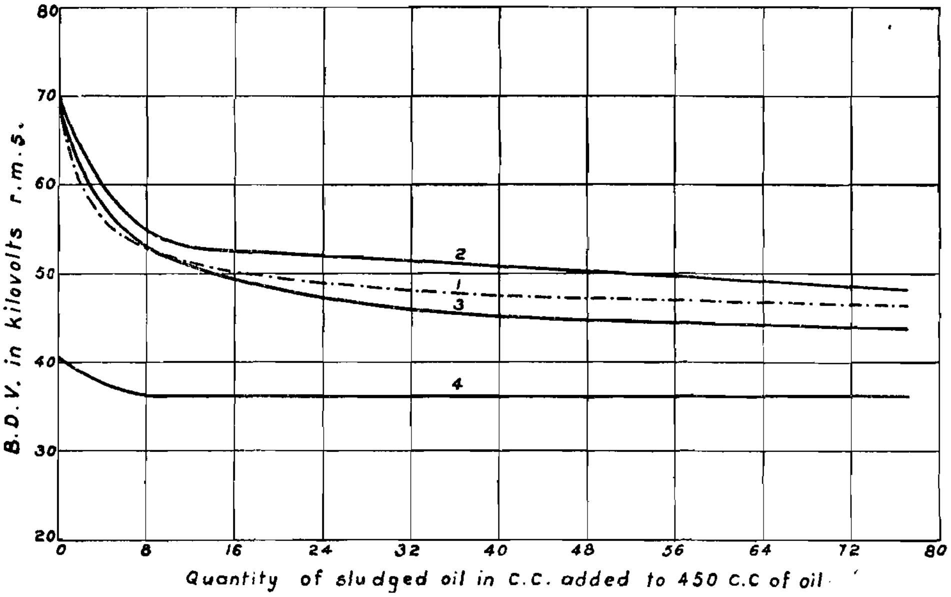

Fig. 10.

Effect of Sludge on the B.D.V. of Transformer Oil.

Effect of mixture of impurities.—Fig. 11 represents the effect of the mixture of sludge, paraffin wax and shellac on the B. D. V. of dry and moist oil. A comparison of these curves with those obtained with shellac shows that the effects are similar and that the lowering of the B. D. V. of oil is approximately the same as that produced by shellac alone. This is to be expected because, of all the impurities tested, shellac produces the maximum change.

Comparison of results for moist oil.—While the curves for dry oil are generally of the same nature, the differences exhibited by the curves for moist oil are interesting. Fig. 12 shows the effect of the various impurities on moist oil having an initial B. D. V. of about 40 kV. 0·15 g. of shellac reduces it to 31·5 kV but beyond this point it remains constant at this value because the effect of further addition of shellac is balanced by the drying of oil due to the discharges. With sludge the

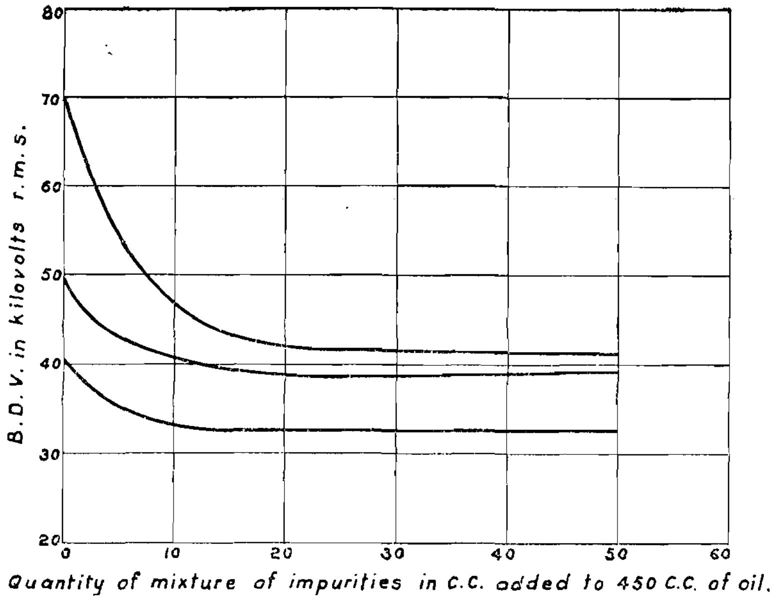

Fig. 11.

Effect of a Mixture of Impurities on the B.D.V. of Transformer Oil.

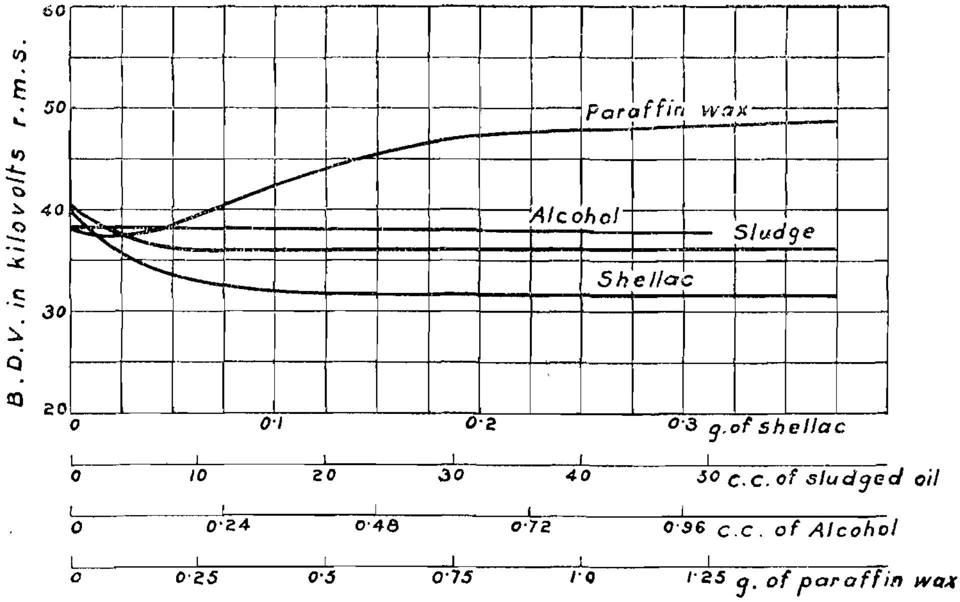

Fig. 12.

Effect of Impurities on the B.D.V. of Moist Transformer Oil.

B. D. V. drops to 36 kV and remains constant at this value. With alcohol there is practically no lowering but a steady value is maintained throughout. With paraffin wax, there is an initial lowering followed by a steep rise due to the preponderating effect of the removal of moisture, and the high value of 49 kV is reached in a comparatively small number of discharges.

CONCLUSIONS.

In dry oils, alcohol, shellac, paraffin wax and sludge do not lower the B. D. V. substantially below 40 kV and therefore do not render it unfit as an insulating medium from the point of view of electric breakdown strength. Of these impurities, shellac and sludge produce the greatest effect even in small quantities. The effect of paraffin wax and alcohol is not so great.

In moist oils the effect of impurities varies considerably with different substances, the greatest effect being produced by shellac and sludge. In the case of paraffin wax the effect of drying is very prominent and the B. D. V. rapidly improves after a small initial drop.

In dry oils the effect of successive discharges after the addition of the impurity is negligible. In moist oils the B. D. V. generally improves and settles down to about 40 kV. Starting from dry or moist oil the final value attained is the same.

The effect of superposition of the impurities is not additive, but the B. D. V. is determined by the impurity which produces the greatest effect.

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BRUSH CONTACT DROP IN D. C. MACHINES.

By M. V. Kesava Rao.

INTRODUCTION.

The characteristics of the voltage drop at the brush contacts in continuous current machines under running conditions have been studied by a number of investigators in view of their great importance as regards sparkless commutation. The main difficulty in an investigation of this nature is to reproduce results under apparently identical conditions, and this difficulty is responsible for the wide disagreement between the results obtained by different experimenters. The object of the present investigation is to determine the influence of the rotation of the commutator on the brush contact drop.

Baily and Cleghorne (*J.I.E.E.*, 1906, **38**, 162) experimenting with slip-rings did not observe any appreciable difference between the values obtained when the slip-rings were stationary and when running at moderate speeds. Arnold (*Die Gleichstrommaschine*, 1910, **1**, 348) obtained similar results with slip-rings. Edgecomb and Dick (*Proc. A.I.E.E.*, 1913, **32**, 451-461) experimented with a short-circuited commutator and observed that the contact drop increased with peripheral speed. Gratzmuller (*La. Lum. Elec.*, 1913, **21**, 324) worked on a commutator with the brushes mounted side by side and in the same axial line, the current passing longitudinally along the segment from one brush to the other. He observed a large increase in the contact drop, amounting to about 100 per cent., as soon as rotation commenced, but the value remained unaltered with speed. An objection to this method pointed out by Hay, Bhatt and Parikh (*J.I.I.Sc.*, 1914–18, **1**, 71) is that the current density over the brush contact area would not be uniform owing to the crowding of the stream lines towards the edges of the brushes facing each other. This objection does not, however, appear to be valid, since the distribution of current over the surface of the brush is mainly determined by the contact resistance, the resistance of the path of current through the commutator segment being comparatively negligible.

Recently, Taylor (*J. I. E. E.*, 1930, **68**, 1356–1362), experimenting with a slip-ring, studied the variation of the contact drop with speed, brush-pressure and current at peripheral speeds higher than those employed by previous investigators. The investigation was also extended to very low current densities and it was observed that when the slip-ring was stationary the contact drop was nearly

proportional to the current; but when it was running, there was a limiting value of the voltage below which no appreciable current could flow. This can be explained by assuming a sudden increase in the voltage drop following the commencement of rotation. Curves connecting contact drop and brush-pressure indicate that the drop decreases with increase of brush-pressure. Curves connecting contact drop with speed for various brush-pressures show that the drop increases slowly up to a certain speed but the rate of increase suddenly rises at that speed. He suggested that the sudden increase at high speeds was due to intermittent contact and the formation of an air film between the brush and the slip-ring.

EXPERIMENTAL.

All experiments with slip-rings suffer from the defect that they do not represent the working conditions in a d-c machine. Consequently, a commutator machine was used in the present investigation.

For the purposes of the experiments, a d-c motor-generator set comprising two similar 5 kW, 220 V, 750 r.p.m., wave-wound rotary converters was used. One of these was used as the machine under test while the other one was used as the driving motor. The armature of each machine had a search coil connected to a pair of slip-rings, so that it was possible to investigate the flux distribution in the air gap under different conditions. The brush-gear was mounted close to the end shield so that there was little vibration in the brushes. There were four brush arms each carrying a brush of 3/8 sq. inch cross section. The full load current density in the brushes was therefore 28 amps./sq. inch. The set was quite new and the commutator had therefore a very smooth surface and the mica was well undercut.

The following method of testing was adopted. Before each set of tests the commutator was carefully cleaned, and the set was run without any current for a sufficiently long time to ensure a proper bedding of the brushes. It was then stopped and a known current was passed through the armature. The total voltage drop between the positive and negative brushes, and the drop in the windings were measured. The difference between the two readings is the sum of the brush resistance and the brush contact drops. As the former is negligible, the difference was taken as the brush contact drop under stationary conditions.

The measurement of contact drop under running conditions required greater precautions, for in this case the total drop between the brushes would include, in addition to the resistance drop, any e.m.f.'s induced in the armature. It was therefore necessary to

arrange the experiments so as to avoid induced e.m.f.'s in the armature. For this purpose, the field poles of the machine under test were removed throughout the tests to obviate e.m.f.'s due to (*a*) asymmetry of the magnetic circuits, and (*b*) the displacement of the brushes from the centre lines of the poles. The e.m.f. due to the rotation of the armature in the earth's magnetic field was measured with a millivoltmeter when the machine was run at full speed in either direction with the field poles removed, and found to be negligible.

Working under similar conditions Hay, Bhatt and Parikh (*loc. cit.*) have concluded as a result of their experiments that the armature was the seat of a counter e.m.f. due to retarded commutation. If such an e.m.f. was present it should be allowed for in calculating the brush contact drop in the present experiments. Consequently, an investigation was made as follows to determine the presence and magnitude of this counter e.m.f.

The following method was adopted by the above investigators to prove the presence of the counter e.m.f. The machine under test, without any current through its armature, was driven by the motor at a definite speed. The motor was separately excited and the input into its armature was measured. When full load current was next passed through the armature of the machine under test and the field and the speed of the motor adjusted to the same values as before, the input into the motor was found to have decreased by about 5 per cent. This was ascribed to a back e.m.f. induced in the machine due to retarded commutation. In the present experiments the same method was adopted but, in order to secure greater sensitivity, a very low voltage supply (5 to 10 v.) was used both for the field and the armature of the motor (Fig. 1).

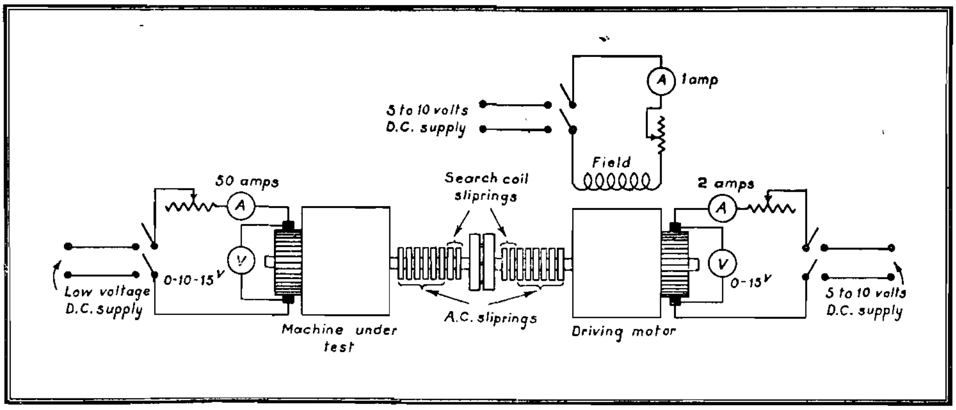

Fig. 1.

Diagram of Connections.

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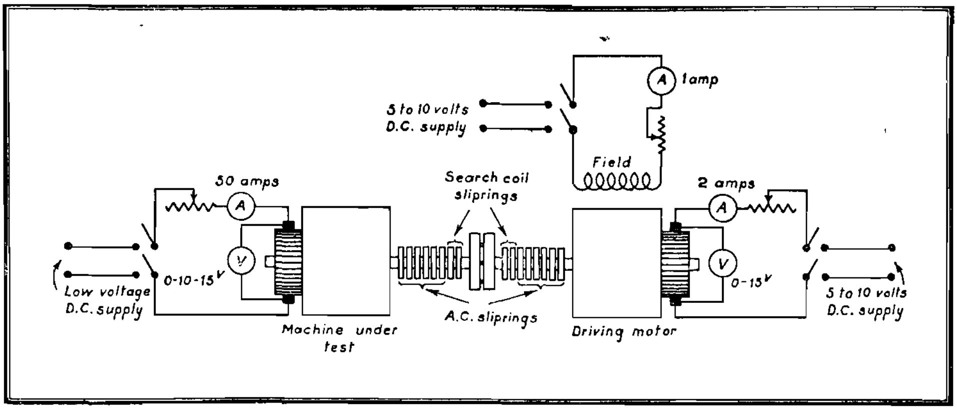

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All experiments with slip-rings suffer from the defect that they do not represent the working conditions in a d-c machine. Consequently, a commutator machine was used in the present investigation.

For the purposes of the experiments, a d-c motor-generator set comprising two similar 5 kW, 220 V, 750 r.p.m., wave-wound rotary converters was used. One of these was used as the machine under test while the other one was used as the driving motor. The armature of each machine had a search coil connected to a pair of slip-rings, so that it was possible to investigate the flux distribution in the air gap under different conditions. The brush-gear was mounted close to the end shield so that there was little vibration in the brushes. There were four brush arms each carrying a brush of 3/8 sq. inch cross section. The full load current density in the brushes was therefore 28 amps./sq. inch. The set was quite new and the commutator had therefore a very smooth surface and the mica was well undercut.

The following method of testing was adopted. Before each set of tests the commutator was carefully cleaned, and the set was run without any current for a sufficiently long time to ensure a proper bedding of the brushes. It was then stopped and a known current was passed through the armature. The total voltage drop between the positive and negative brushes, and the drop in the windings were measured. The difference between the two readings is the sum of the brush resistance and the brush contact drops. As the former is negligible, the difference was taken as the brush contact drop under stationary conditions.

The measurement of contact drop under running conditions required greater precautions, for in this case the total drop between the brushes would include, in addition to the resistance drop, any e.m.f.'s induced in the armature. It was therefore necessary to

arrange the experiments so as to avoid induced e.m.f.'s in the armature. For this purpose, the field poles of the machine under test were removed throughout the tests to obviate e.m.f.'s due to (*a*) asymmetry of the magnetic circuits, and (*b*) the displacement of the brushes from the centre lines of the poles. The e.m.f. due to the rotation of the armature in the earth's magnetic field was measured with a millivoltmeter when the machine was run at full speed in either direction with the field poles removed, and found to be negligible.

Working under similar conditions Hay, Bhatt and Parikh (*loc. cit.*) have concluded as a result of their experiments that the armature was the seat of a counter e.m.f. due to retarded commutation. If such an e.m.f. was present it should be allowed for in calculating the brush contact drop in the present experiments. Consequently, an investigation was made as follows to determine the presence and magnitude of this counter e.m.f.

The following method was adopted by the above investigators to prove the presence of the counter e.m.f. The machine under test, without any current through its armature, was driven by the motor at a definite speed. The motor was separately excited and the input into its armature was measured. When full load current was next passed through the armature of the machine under test and the field and the speed of the motor adjusted to the same values as before, the input into the motor was found to have decreased by about 5 per cent. This was ascribed to a back e.m.f. induced in the machine due to retarded commutation. In the present experiments the same method was adopted but, in order to secure greater sensitivity, a very low voltage supply (5 to 10 v.) was used both for the field and the armature of the motor (Fig. 1).

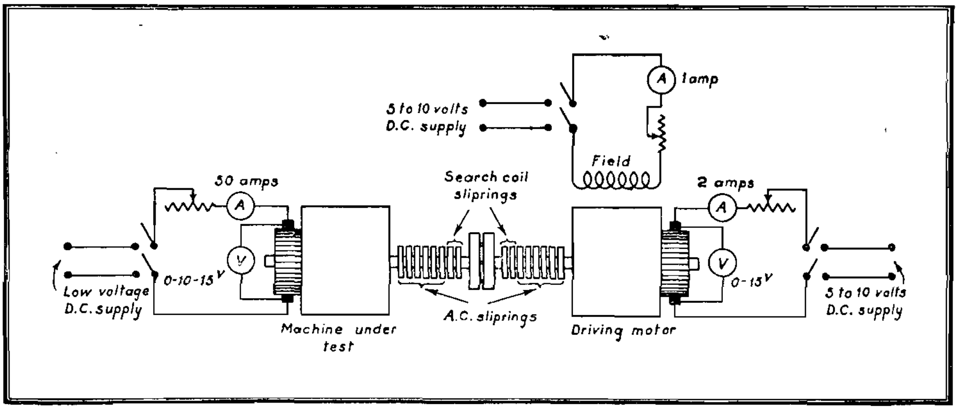

Fig. 1.

Diagram of Connections.

The input into the motor armature balanced its no-load losses (friction, windage and iron losses) and armature copper loss. The reduction of input due to the counter e.m.f. in the armature under test was a small fraction of the input. Consequently, by using a low field voltage the iron losses were reduced and greater sensitivity obtained. By using a low armature voltage, the armature current was correspondingly increased and could be measured with a high degree of accuracy. With this arrangement, it was possible to detect a change in the input of the order of 1 part in 500, but no change was observed even with speeds up to 900 r.p.m. and currents up to twice the full load current of the machine.

In order to verify the result, the following retardation method was adopted (Fig. 2). The set was run up to a definite speed without any current through the armature under test. The armature and field supply of the motor was next switched off and the rate of retardation observed. The experiment was then repeated with a known current through the armature under test.

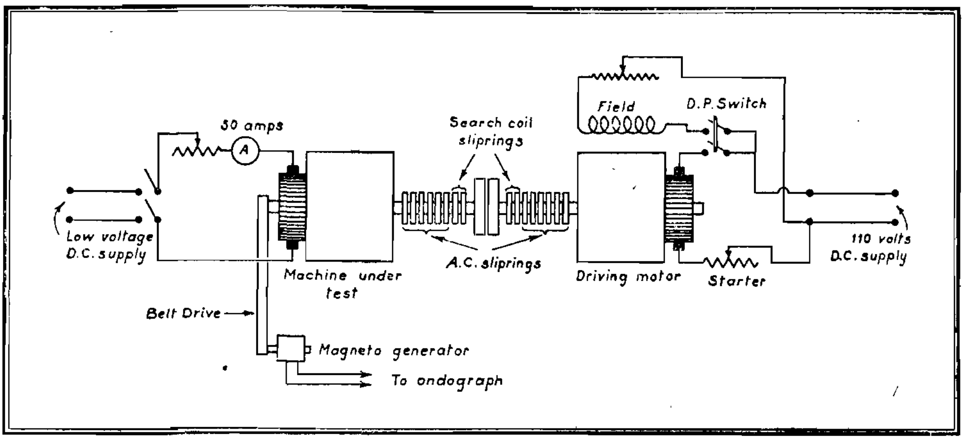

Fig. 2.

Diagram of Connections for Retardation Test.

A counter e.m.f. in the armature under test would give rise to a motoring torque, and consequently the retardation of the set would be reduced and it would take longer to come to rest. The retardation in each case was recorded by means of an ondograph. A magneto-generator was belted to the set so that the variation of its e.m.f. was a measure of the variation of the speed of the set. The e.m.f. was applied to the galvanometer of the ondograph of which the drum was driven at a constant speed by supplying its synchronous motor from a source of constant frequency. On superposition, the two retardation curves obtained with and without current through the armature under test coincided exactly, indicating an absence of an induced e.m.f. in the armature. This confirmed the result obtained previously by the other method. The arrangement was sensitive enough to record changes in the torque of the order observed by the above investigators.

It is, however, possible that the counter e.m.f. in the armature was just enough to balance the additional losses in the armature core due to its rotation in its own stationary field. Another experiment was therefore carried out to determine the order of this loss. The wave shape of the flux due to the armature current was traced by means of an oscillograph connected to the search coil, the oscillograph motor being supplied from the motor slip-rings. The nature of the oscillogram is shown on Fig. 3 and shows a number of ripples which increase in amplitude as the crest of the wave is approached. The nature of the ripples indicates that they are due to voltages induced in the search coil by mutual induction with coils undergoing short-circuit, the mutual induction being greatest when the search coil comes into line with the brushes, and therefore with the coils undergoing short-circuit. The induced voltage can therefore be resolved into two components: (*a*) the dotted curve representing the effect of rotation in the armature flux, and (*b*) the ripples superposed on it, due to mutual induction.

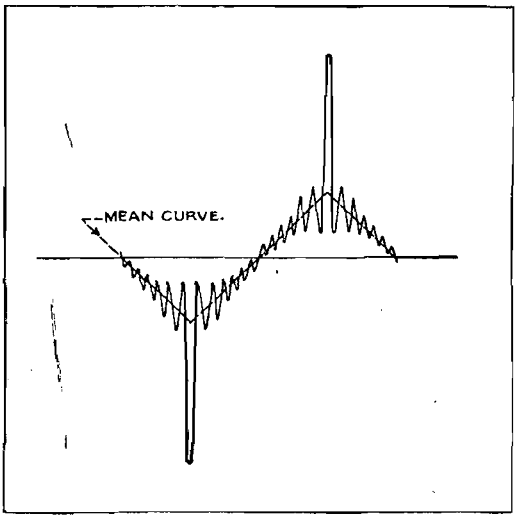

Fig. 3.

Flux Wave due to Armature Current with Field Poles removed. Armature Current 40 Amp. Speed 900 r.p.m.

The dotted curve is a measure of the maximum induction due to armature current. The next point was therefore to determine whether the hysteresis and eddy current losses due to this value of induction could absorb any appreciable counter e.m.f. For this purpose, the field poles were replaced and the set was run again at the same speed as before without any current through the field or armature of the machine under test, and the motor input was noted. The field of the machine under test was now excited so as to produce the same value of maximum induction as that produced by the armature current in the previous test, this condition being determined by the oscillograph. The motor input was again noted. The difference between the two values of the motor input gives the iron losses corresponding to the value of induction. It was found that even for armature current equal to twice the full load current and at the maximum permissible speed (900 r.p.m.), the loss was of the order of 5 watts and the corresponding back e.m.f. negligible as compared with the contact drop.

All this proves that there is no appreciable counter e.m.f. in the armature and, neglecting the brush resistance drop, the difference between the total drop and the armature drop can be taken as being equal to the contact drop.

However, the contact drop is very largely affected by the nature of the surface of the commutator as can be seen from the following experiment. The commutator was polished and the contact drop measured by passing a known current when the machine was stationary. The commutator was next blackened by passing a large current through it and running the machine for some time. The machine was stopped and the contact-drop measured with the same current as before. The drop was found to be considerably reduced. The commutator was again polished and on measuring the drop again with the same current, it was found that it had increased to more or less the same value.

Consequently, it is essential that in tests for determining the increase of contact-drop due to rotation, involving alternate readings at stand-still and under running conditions, the nature of the commutator surface should remain unchanged as far as possible between each pair of readings. In order to approximate to this condition as far as possible the following procedure was adopted: (1) A definite value of current was passed through the armature under test at stand still and the voltage drop measured. (2) The current being maintained at the same value, the armature was driven at the required speed and the drop measured again. (3) The current being still maintained at the same value, the armature was again brought to rest and the drop measured once more. All the three readings were taken as quickly as possible in order to minimise the change in the nature of commutator surface. The mean of readings 1 and 3 was taken as the drop under stationary condition, and was deducted from the drop obtained in reading 2 in order to obtain the increase of drop due to rotation. A set of readings corresponding to a definite speed and increasing values of current was first taken, and similar sets were then obtained at different speeds. At the beginning of each set the commutator was cleaned.

Fig. 4 represents the variation in the value of "the stationary drop". The stationary drop corresponding to a definite speed represented by each of the curves in the figure is the mean value of readings 1 and 3 obtained for that speed, plotted against the varying current. It will be seen that the stationary drop at zero speed is represented by the highest curve while the stationary drops at other speeds become smaller as the speed increases. This is due to the greater blackening, and consequently lower drop, at increasing speeds. The reduction in the voltage drop with increase of speed is very great at first but becomes smaller until it seems to become very small at about 750 r.p.m. These curves bring out the extreme importance of obtaining the change in contact drop from a pair of readings obtained under similar conditions of commutator surface.

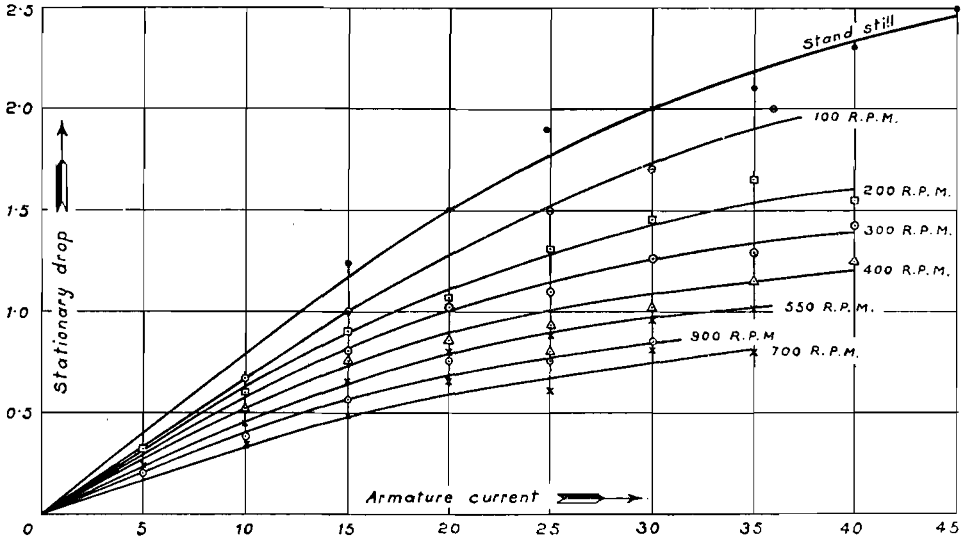

Fig. 4.

Effect of Commutator Surface on Contact Drop.

Fig. 5 represents the increase of voltage drop due to speed. At each value of speed, the drop initially increases in direct proportion to the current, but the rate of increase becomes smaller until it finally tends to reach a constant value. This constant value is, however, not reached with the maximum current used in the experiment. It was not possible to push the current up to higher values due to sparking.

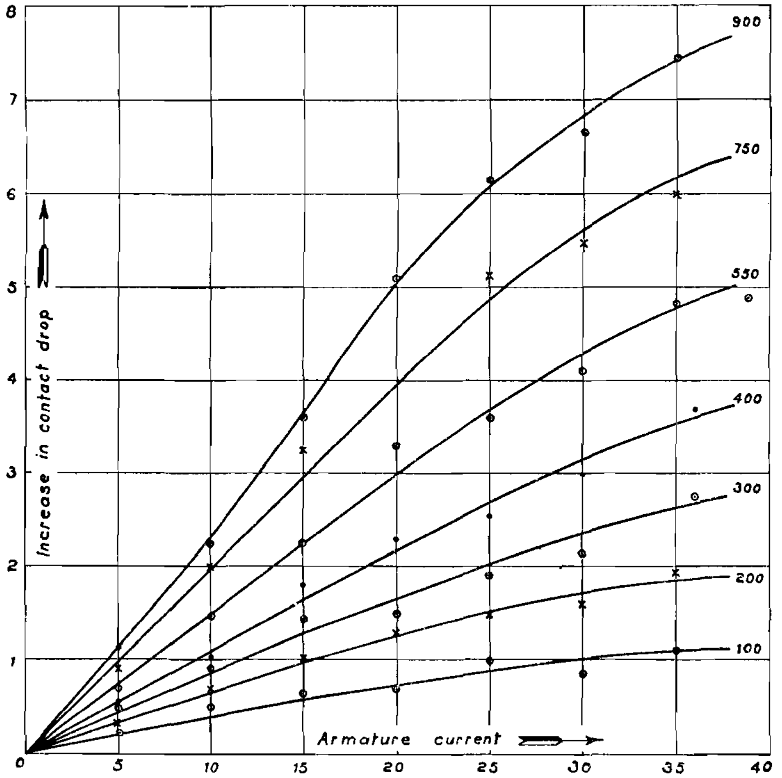

Fig. 5.

Increase of Brush Contact Drop due to Speed.

For a definite value of the current, the increase in contact drop increases with speed. Fig. 6, derived from Fig. 5, represents the effect of increasing speeds with definite values of current and indicates that, with constant current, the increase in drop increases in direct proportion to the speed.

It is believed that these results represent more correctly the effect of speed on the brush contact drop than those obtained by previous investigators. Most of them have worked with slip-rings instead of commutator, while those who have worked with the commutator do not seem to have realised the importance of the error due to the change in the surface of the commutator during each set of their experiments.

Observations were also made to ascertain if the "stationary contact drop at zero speed" could be reproduced from day-to-day and the results shown on Fig. 7 indicate that it could be reproduced with reasonable accuracy on different days provided the commutator was well cleaned at the beginning of each set of readings.

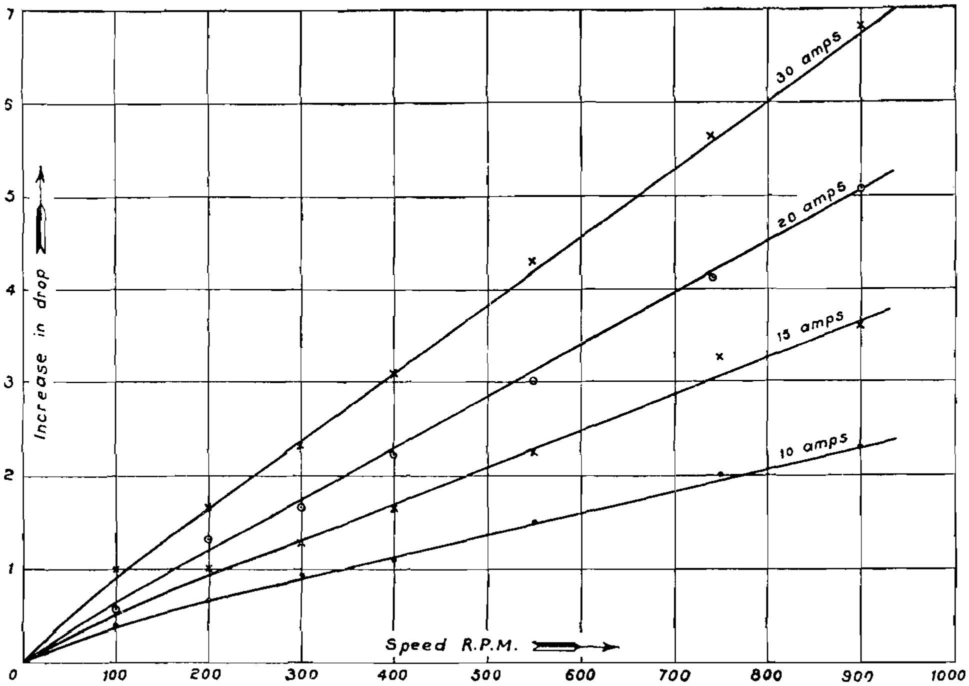

Fig. 6.

Increase of Brush Contact Drop due to Speed.

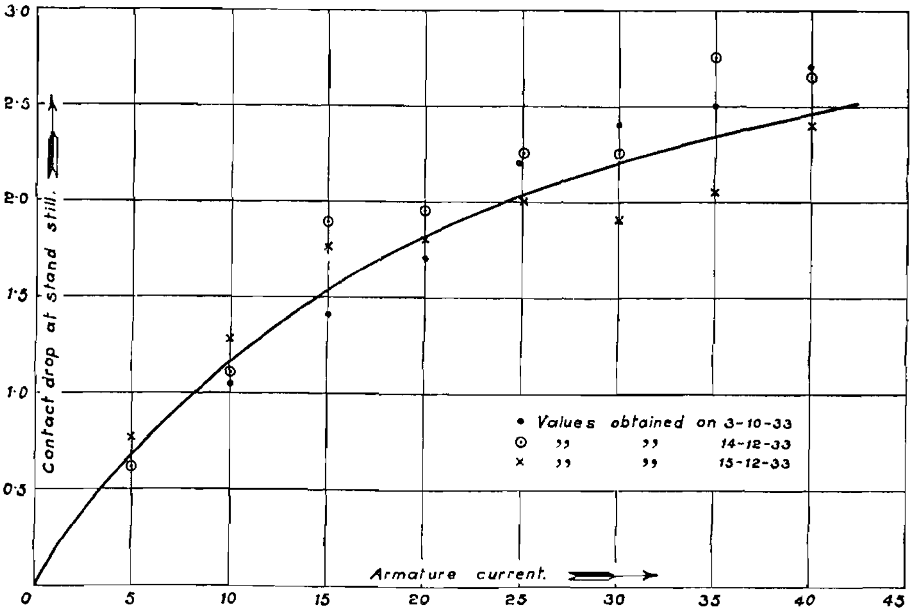

Fig. 7.

Contact Drop at Stand Still.

CONCLUSIONS.

The investigation brings out the following results :—

(1) The contact drop between the commutator and the brush is capable of being reproduced fairly satisfactorily on different days, if care is taken to clean the commutator before each set of observations.

(2) The effect of blackening of the commutator due to the passage of current, when the commutator is running, is very large and may produce considerable errors in the observations, unless duly allowed for.

(3) No counter e.m.f. due to retarded commutation was observed.

(4) The brush contact drop increases with increasing speed. For the same value of speed, the increase is initially in direct proportion to the current but tends to a constant value at very high currents. With constant current, the increase is in direct proportion to the speed upto the maximum speeds experimented with.

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THE POTENTIAL OF DRY CELLS WITH MAGNESIUM CHLORIDE ELECTROLYTE.

By V. L. R. Vepa.

INTRODUCTION.

The type of dry cell which is most used contains 20 to 25% of ammonium chloride solution, a little zinc chloride and often some calcium chloride. These cells are found unsatisfactory in tropical climates chiefly due to:—(*a*) creeping of ammonium chloride which not only results in a loss of electrolyte but also in the corrosion of the brass cap of the cell, and (*b*) the drying up of the electrolyte which retards the chemical action of the cell and lowers its life. To avoid these defects several organic as well as inorganic chemicals[1,2,3] have been tried to replace the ammonium chloride in the cell. Of these, magnesium chloride has found favour not only due to its greater hygroscopic properties but also its cheapness as compared with ammonium chloride. Besides this, it has been found that magnesium chloride cells give higher initial e.m.f., greater service, and longer shelf life as compared with ammonium chloride cells.

The potential of an electrode is largely determined by the nature and the pH value of the electrolyte in which it is immersed. So far, the importance of pH variation in dry cells has not been fully investigated and only a few papers [4,5,6,7,8] have been published which deal with this subject but most of these relate to cells with ammonium chloride as electrolyte. Martin and Helfrecht[6] found that the P.D. between the manganese dioxide—carbon electrode and 20% ammonium chloride solution varied from 0·3760 to 0·2903 as pH value of the solution was varied from 1·2 to 7·9, *i.e.*, a change in potential of 0·086 volt for a change in pH of 6·7. Owing to the suitability of

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[1] Thompson and Crocker, *Trans. Am. Electrochem. Soc.*, 1915, **27**, 155.

[2] Kostjejev, *Trans. Am. Electrochem. Soc.*, 1930, **58**, 305.

[3] Felix Kainz, *Chemiker-Zeitung*, 1932, **56**, 691.

[4] Holler and Ritchie, No. 364, Scientific Paper, *Bull. B. Stds.*, 1919-20, **15**, 659.

[5] Farrington Daniels, *Trans. Am. Electrochem. Soc.*, 1928, **53**, 52.

[6] Martin and Helfrecht, *Ibid.*, 1928, **53**, 83.

[7] Allmand, *Applied Electrochemistry*, 1924, p. 213.

[8] Keller, *Zeits. f. Electrochem.*, 1931, **37**, 342–348.

magnesium chloride cells for tropical climates and the absence of data relating to the variation of P. D. with pH of the electrolyte, this investigation was undertaken to examine the variation of P. D. of cells containing magnesium chloride electrolyte of various pH values.

EXPERIMENTAL.

Preparation of Electrode.—For experiments given here, Indian pyrolusite ore of 60 to 80 mesh containing 76% of manganese dioxide and flake graphite containing 97% of carbon were used. The carbon rods were each of 55 mm. length and 10 mm. diameter. Finished core was of 35 mm. diameter and 40 to 42 mm. high. The proportions, by weight, in this bobbin were 4 parts of pyrolusite ore to 1 part of flake graphite. The mass was wetted with a small amount of distilled water to facilitate moulding. It was tamped around a carbon rod under hydraulic pressure which was gradually raised up to 800 lbs. per square inch and the whole mass was then wrapped in a muslin cloth. The electrodes were then dried for 48 hours in a current of hot air, at about 100°C. obtained from an electrically operated air oven. A copper wire was soldered to the brass cap fitted on to the carbon rod to serve as a lead to the potentiometer terminal.

Preparation of Solutions.—Solutions of magnesium chloride having concentrations of 15, 20, 25 and 50% were prepared. Then solutions of different pH values from strongly acidic (pH 1 to 2) to slightly alkaline (pH 7 to 8) were obtained by adding definite amounts of acid or alkali to the above solutions.

Method of Measurement.—The pH value of the electrolyte in which manganese dioxide—carbon electrode was immersed was first determined with the help of quin-hydrone electrode. Next the potential of the electrode itself was measured against the saturated calomel cell in the solutions described above.

The schematic representation of the arrangement used in this set of experiments is: —

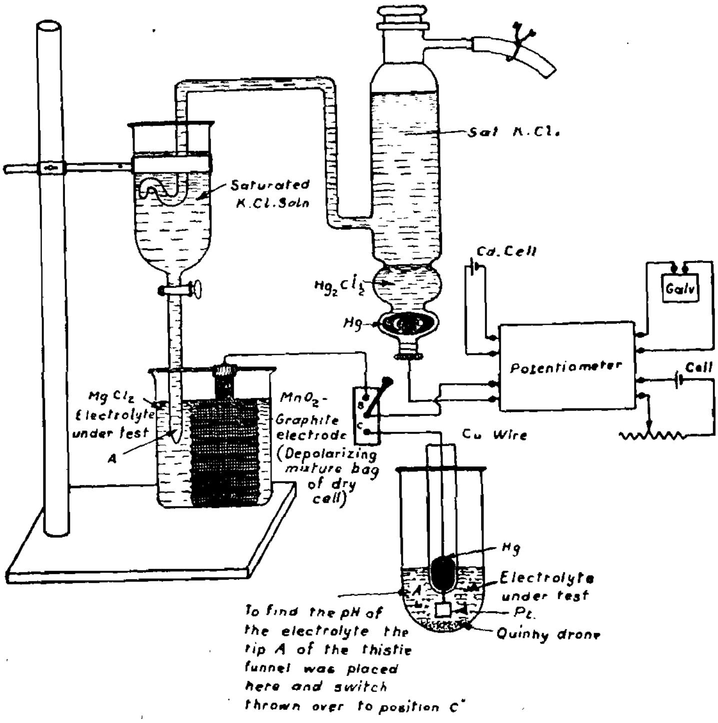
$$\mathrm{Hg} \;\Big|\; \mathrm{HgCl} \;\Big|\; \begin{array}{c}\text{Sat. KCl}\\ \text{solution}\end{array} \;\Big|\; \begin{array}{c}\mathrm{MgCl_2}\text{ of}\\ \text{known }(\mathrm{H^+})\\ \text{concentration}\end{array} \;\Big|\; \mathrm{MnO_2\text{–}C}$$

The e.m.f. of this chain was measured with the potentiometer. The pH of the electrolyte was calculated from the potentiometer reading by using the well-known formula:

$$\mathrm{pH} = \frac{E - E_{\mathrm{std.}} - E_{\mathrm{obs.}}}{0{\cdot}058}$$

where $E = (0{\cdot}7175 - 0{\cdot}00075\ t\,^{\circ}\mathrm{C.})$ volts.

The apparatus used is shown diagrammatically in Fig. 1.



To find the pH of the electrolyte the tip A of the thistle funnel was placed here and switch thrown over to position C'

Fig. 1.

The arrangement of apparatus set up to measure the pH of magnesium chloride electrolytes and the P. D. of the manganese dioxide—carbon electrode.

Test Results.—Curves 1, 2, 3 and 4 in Fig. 2 show the results obtained from tests for magnesium chloride solutions of strength marked against the respective curves. Curve 5 in Fig. 2 is reproduced from a paper by Martin and Helfrecht[6] for comparison, as it relates to an electrode composed of caucasian pyrolusite ore containing 74·8% manganese dioxide which is nearest to the ore (76% manganese dioxide) used in the present experiments. The electrolyte used by Martin and Helfrecht was 20% ammonium chloride solution.

Variation of Potential with pH.—An examination of the curves in Fig. 2 shows that all the cells have a common characteristic, *viz.*, rapid falling of potential for pH values 1 to 3, a slight variation for pH values 3 to 6·5, a pronounced rise in every case for a pH value of about 6·5 and then again a rapid fall on entering the alkaline region. It is interesting to note that for all the four solutions tested, the maximum potential occurs at a value of pH lying between 0·75 and 1·5, and the point of maximum potential occurs further up on the pH scale as the percentage concentration of the solution is decreased.

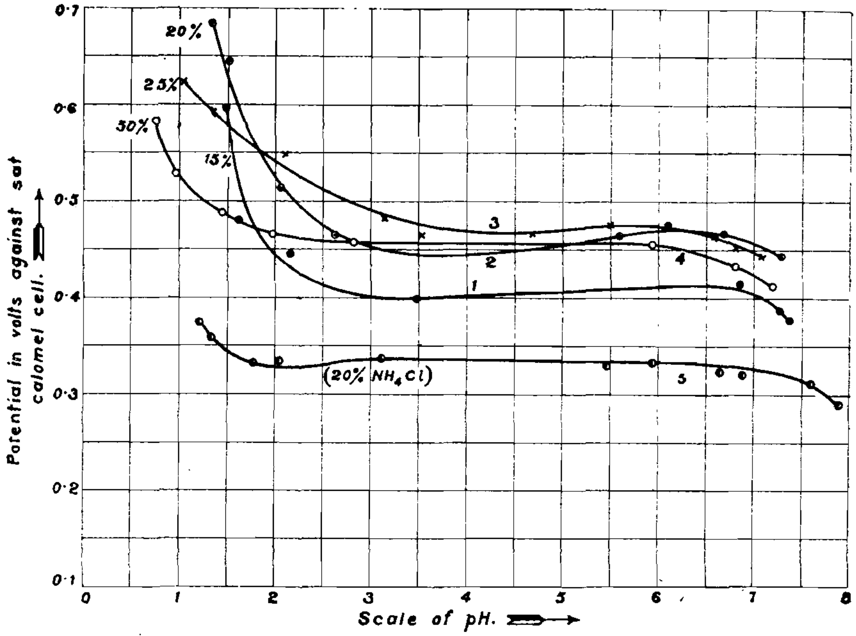


Fig. 2.

Graphs showing the variation in potential of manganese dioxide—carbon electrode with pH and strength of electrolyte.

It will be observed that with highly acidic solutions, a high initial potential is obtained but this is offset by the rapid drop in potential as the pH value approaches 2·5, and the destructive effect of the solution on the zinc of the cell. From considerations of steady potential and for minimising the corrosive effect of the electrolyte, it is advisable to start with a pH value of about 2·5. Comparing the four cells in the region of pH 2·5 to 6·5 which appears to be the most suitable working range, it will be seen that the maximum potential is obtained with 25% solution and the variation of potential during the life of this cell is quite satisfactory. A decrease in the strength of solution results not only in a decrease in the maximum potential but also a greater variation of potential during the life of the cell. With a 50% solution the potential is steadier during the life of the cell than with other solutions but the average potential is the lowest.

From considerations of economic production, high initial voltage and steady P. D. of the cell during its active life, it would appear that 25% solution is the most suitable.

CONCLUSIONS.

1. Average potential during the life of a magnesium chloride cell is higher than that of an ammonium chloride cell.

2. Maximum potential and change of potential during the life of a cell varies with the strength of the electrolyte.

3. From considerations of economic production, high initial voltage and steady P. D. of the cell during its active life, 25% solution is the most suitable.

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