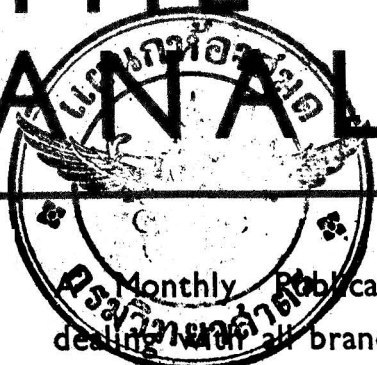




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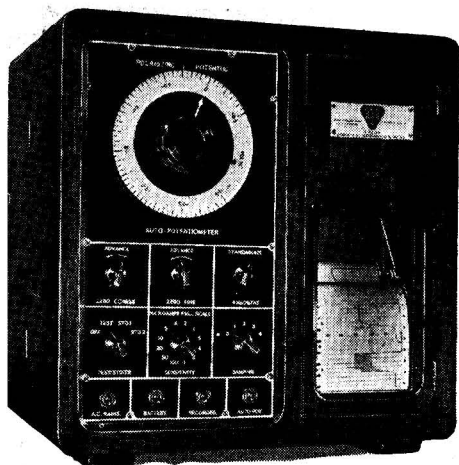
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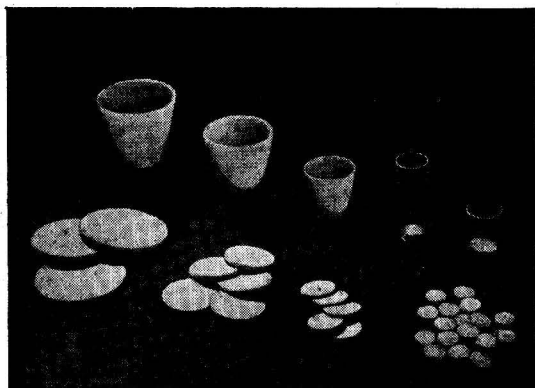
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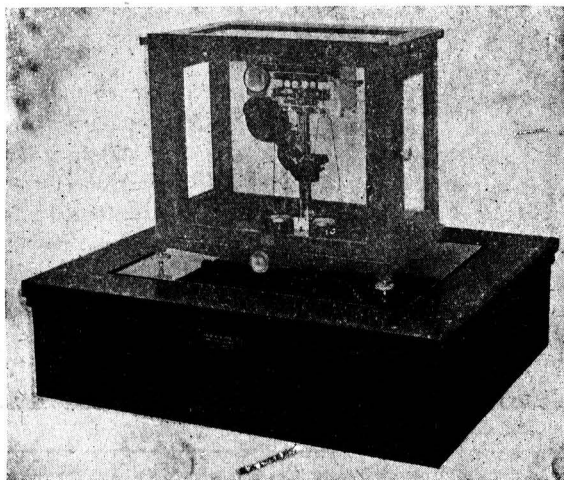
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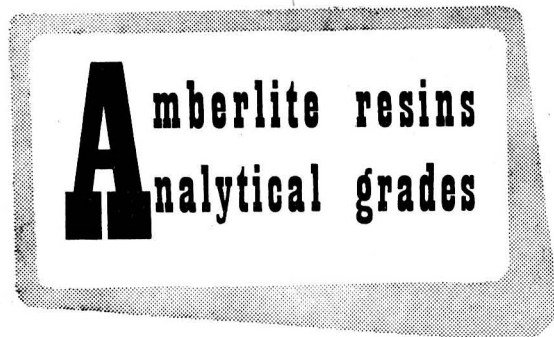
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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, November 1st, 1950, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The chair was taken by the President, Mr. George Taylor, O.B.E., F.R.I.C.

The following papers were presented and discussed: "Chemical Determination of Magnesium in Cast Iron," by W. Westwood, B.Sc., A.I.M., and R. Presser; "The Determination of Sodium in Aluminium and its Alloys by Vacuum Distillation," by W. McCamley, B.Sc., T. E. L. Scott and R. Smart, B.Sc., A.R.I.C.; "The Determination of Lead Oxide in the Presence of Lead," by R. M. Black, M.Sc., A.R.I.C.

DEATH

We deeply regret to record the death of
Bernard Scott Evans.

BIOLOGICAL METHODS GROUP

A MEETING of the Group was held at 2.30 p.m. on Tuesday, October 24th, 1950, at the Medical Society of London, Chandos Street, Cavendish Square, London, W.1. Mr. N. T. Gridgeman, B.Sc., A.R.I.C., the Chairman of the Group, occupied the chair.

The meeting took the form of a Symposium on the Biological Assay of Adrenocorticotrophic and Cortical Hormones. The following papers were presented and discussed: "Technique of Hypophysectomy and Adrenalectomy in Mammals," by M. Pickford; "The Adrenal Ascorbic Acid Depletion and Adrenal Repair Methods for the Bio-Assay of ACTH," by C. J. O. R. Morris; "ACTH Assay: Experiences with the Ascorbic Acid Depletion Method and Comparison with Preliminary Observations on the Use of the Inhibition of Tissue Repair," by B. E. Clayton and F. T. G. Prunty; "Assay of Cortical Hormones on Small Laboratory Animals," by M. Vogt; "Methods in the Evaluation of Adrenocorticotrophic and Cortical Hormones in Man," by E. G. L. Bywaters.

PHYSICAL METHODS GROUP

THE Twenty-seventh Ordinary Meeting of the Group was held at 5.30 p.m. on Friday, October 6th, 1950, in the Council Chamber of the Municipal Buildings, Poole, Dorset. This was a joint meeting with the Mid-Southern Counties Section of the Royal Institute of Chemistry. Mr. B. S. Cooper, the Chairman of the Group, and Dr. J. M. Wright, the Chairman of the Mid-Southern Counties Section of the R.I.C., jointly occupied the chair; about fifty-six members and visitors were present.

The following papers on Flame Photometry were read and discussed: "Flame Photometers—a Description of Two Instruments," by L. Brealey, B.Sc., and R. E. Ross; "Notes on the Internal Standard Technique (in Flame Photometry) with Special Reference to Solution Filters," by T. C. J. Ovenston, B.Sc., Ph.D., F.R.I.C., and A. M. Robinson; "The Rapid Determination of Sodium and Potassium in Rocks and Minerals," by G. H. Osborn, F.R.I.C., A.M.Inst.M.M., and H. Johns, B.Sc.

MICROCHEMISTRY GROUP

THE Autumn meeting of the Group was held jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry on Wednesday, September 27th, 1950.

During the afternoon a tour was made of the new Research Centre of Messrs. Dunlop Rubber Company at Fort Dunlop.

Following tea at the University Refectory, Edmund Street, a symposium on "The Micro-analytical Chemistry of Fluorine" was held in the Mason Theatre of the University.

The following papers were contributed: "Analysis of Organic Fluoro-Compounds," by F. P. Johnson; "Micro-determination of Carbon and Hydrogen in Fluoro-Compounds," by W. T. Chambers; "A Study of the Potentiometric Titration of Fluoride with Lead," by F. R. Cropper; "Demonstration of a Multiple Apparatus for the Determination of Micro Quantities of Fluorine," by R. F. Milton.

A Collaborative Study of the Freezing-Point Depression (Hortvet) of Sucrose Solutions

BY R. ASCHAFFENBURG AND J. KING

DURING the last few years a committee of the British Standards Institution has been engaged in preparing a standard method of determining the freezing-point depression of milk. Some of the directions given by Hortvet¹ have in the past been interpreted in different ways. It was, therefore, necessary to formulate the Hortvet technique in more precise terms to ensure a higher degree of reproducibility, and this was done by a sub-committee. The details of the technique arrived at, and recommended for incorporation in a British Standard, are given below. To ascertain that satisfactory reproducibility was obtained when a number of laboratories followed the recommended procedure, a collaborative experiment was arranged by the following—

Government Laboratory (Mr. J. King and Dr. H. Egan)
Dr. Bernard Dyer and Partners (Dr. J. H. Hamence)
National Institute for Research in Dairying (Dr. R. Aschaffenburg)
Messrs. Cow & Gate Limited (Mr. H. C. Hillman)
The Hannah Dairy Research Institute (Dr. R. Waite)
Milk Marketing Board (Dr. A. L. Provan and Mr. F. J. Macdonald)
Lancashire County Council (Dr. G. H. Walker).

The collaborating laboratories were asked to determine the freezing-point depression of an 8.5 per cent. (w/v at 20°C) solution of sucrose with thermometers calibrated at the National Physical Laboratory, applying the corrections given on the certificates as recommended by Aschaffenburg and Hall.² These authors have confirmed the experience of many observers that it is difficult to obtain uniform results with sucrose solutions of 10 per cent. or even lower concentration. It did, however, seem reasonable from their findings that a solution of 8.5 per cent. could be expected to give uniform results that should be in accordance with those interpolated by Elsdon and Stubbs^{3,4} in this country from the work of Hortvet¹ in the U.S.A., since these observers used thermometers calibrated on the International Temperature Scale at the National Physical Laboratory and the Bureau of Standards, respectively, as their standards of temperature.

The seven laboratories were requested to carry out four determinations of the freezing-point of an 8.5 per cent. solution of sucrose and two determinations for water (one value before and one after the sucrose solutions) with either the Hortvet or the Temple cryoscope. When the latter was used, the motors driving the stirrer and the compressor were to be switched off at the time of seeding. Any result considered unsatisfactory was to be recorded separately. Pure A.R. sucrose prepared from cane sugar was sent to all participating laboratories.

TABLE I
SUMMARY OF COLLABORATIVE RESULTS

Laboratory	Apparatus	Thermometer No.	Corrected maximum temperature reading						Freezing-point depression (mean), °C	Remarks
			8.5% sucrose solution			Water				
			Lowest, °C	Highest, °C	Mean, °C	1st test, °C	2nd test, °C			
A	Hortvet	33988	-0.523	-0.520	-0.521	-0.001	-0.001	0.520		
B	"	"	-0.520	-0.516	-0.5175	+0.005	+0.004	0.522	Thermometer on loan from Laboratory A	
B	"	"	-0.517	-0.516	-0.5165	+0.004	+0.004	0.5205		
C	"	62652	-0.530	-0.526	-0.528	-0.008	-0.005	0.5215	Two sets of results on different days	
C	"	17424	-0.520	-0.519	-0.520	-0.003	-0.002	0.5175		
D	Temple	46611	-0.520	-0.517	-0.519	+0.002	+0.002	0.521		
D	"	4839044	-0.519	-0.517	-0.5185	+0.001	0.000	0.519		
E	"	69279	-0.508	-0.507	-0.5075	+0.010	+0.011	0.518		
F	"	4839004	-0.533	-0.531	-0.532	-0.012	-0.012	0.520		
G	Hortvet	3710288	-0.513	-0.512	-0.5125	+0.009	+0.008	0.521	Standard deviation = 0.0015 Thermometer not N.P.L. standardised, uncorrected thermometer readings	
								General mean:		

EXPERIMENTAL PROCEDURE

FREEZING-POINT OF 8.5 PER CENT. SUCROSE SOLUTION—

Cool with prescribed rate of stirring⁵ (1 complete stroke per 1 to 2 seconds) until the temperature of the sucrose solution reaches -1.65°C . Insert freezing starter tube holding ice fragment. Stir at prescribed rate until the mercury thread rises. Immediately remove freezing starter tube and cease stirring. After about 90 seconds the apparent highest temperature should be reached. Then stir three times at normal speed, tap the thermometer stem seven times at the level of the top of the mercury thread and read the thermometer. Thirty seconds after this reading, stir again three times followed by tapping seven times as before and again read. Repeat these operations a third time and record the final reading. The difference between the first and second reading may exceed 0.005°C but does not usually exceed 0.01°C ; there should not be a greater difference than 0.003°C between the second and third readings. When the difference is greater, the result should be discarded and the test repeated.

FREEZING-POINT OF WATER—

Carry out the procedure as above, but if freezing is not spontaneous, insert the freezing starter tube at -1.1°C .

RESULTS

The results obtained by the seven laboratories are summarised in Table I. For each set of determinations, the range and mean value for 8.5 per cent. sucrose solution, and the two values for water, are listed together with the mean value for the freezing-point depression of the sucrose solution. No abnormal results were reported other than those due to insufficient super-cooling or abnormal outside bath temperatures. Table I shows that it is possible for different laboratories to obtain uniform results by following the recommended procedure. A wider range was obtained when each laboratory used its own technique.

The mean for all results obtained by the technique given above is identical with the value of 0.520°C given by Stubbs and Elsdon.⁴ All but one of the mean values for the individual sets of results fall within $\pm 0.002^{\circ}\text{C}$ of the general mean. This is well within the accuracy to which Hortvet thermometers are calibrated at the National Physical Laboratory. It will also be seen that the results obtained with the Temple apparatus are indistinguishable from those obtained in the Hortvet cryoscope.

These results from seven laboratories were obtained before the publication of the paper by Sutton and Markland.⁶ They are not in accordance with the experience of these authors.

Four of the laboratories have extended the work to more concentrated sucrose solutions of 9.0 and 8.75 per cent. The results with 9.0 per cent. solutions confirmed that values are less uniform at this level of concentration. With 8.75 per cent. solutions no difficulties were encountered, although they might have been expected from the data of Aschaffenburg and Hall.²

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4. Stubbs, J. R., and Elsdon, G. D., *Ibid.*, 1936, **61**, 455.
5. Hortvet, J., *J. Ass. Off. Agric. Chem.*, 1921, **5**, 175.
6. Sutton, R. W., and Markland, J., *Analyst*, 1950, **75**, 251.

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October, 1950

A Review of Some Developments in the Use of the Karl Fischer Reagent

BY A. G. JONES

(Presented at the meeting of the Society on Wednesday, February 1st, 1950)

Some recent developments in the use of the Karl Fischer reagent are surveyed under the headings of composition and preparation of the reagent, method of titration and determination of the end-point, and the versatility of the reagent. The relationship between various theoretical equations and the practical findings are examined, the advantages and disadvantages of using the Fischer reagent in two solutions are discussed, and a few applications of the reagent are mentioned.

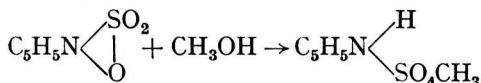
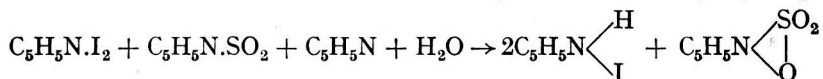
THE determination of moisture has now been dignified with the title of "Aquametry" by the Americans, and the book of that name written by Mitchell and Smith¹ gives a comprehensive survey of the uses of the Karl Fischer reagent. However, a review of some of the more important developments in the use of the reagent should be of general interest. The subject may be considered under three main headings: (i) the composition and preparation of the reagent; (ii) the method of titration and determination of the end-point; and (iii) the versatility of the Fischer method.

THE COMPOSITION AND PREPARATION OF THE REAGENT

The Fischer reagent is a solution of iodine, sulphur dioxide and pyridine in dry methanol. The dark brown colour of this solution is discharged when a sample containing water is titrated with it, the end-point of the titration being reached when the brown colour of the reagent persists. Karl Fischer² believed this reaction to require two molecules of water for every molecule of iodine present in accordance with the equation—



However, Smith, Bryant and Mitchell³ considered that only one molecule of water reacted with one molecule of iodine according to the following equations—

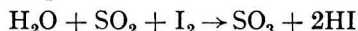


It has been found by numerous workers that the theoretical efficiency of this second set of equations is never attained. The freshly prepared reagent is usually equivalent to about 80 per cent. of its theoretical strength, but in a month that equivalence falls to 50 per cent. and in three months it is only about 40 per cent. This deterioration is due partly to reaction with the water present in the chemicals used to prepare the reagent, but mainly to various side reactions that take place. As a result the Fischer reagent must be standardised very frequently, and this must be regarded as a limitation of the method.

There is little difficulty in obtaining iodine, methanol and sulphur dioxide of a quality suitable for preparing the Fischer reagent, but Almy and his colleagues⁴ noted that some grades of pyridine gave a reagent of inferior quality when compared with others.

Another limitation or inconvenience in the use of the Fischer reagent is the presence of water vapour in the atmosphere, and elaborate precautions must be taken to prevent contamination of the reagent either before or during a titration. The possibility of contamination by atmospheric moisture together with the deterioration of the reagent on standing has caused those who have need to store quantities of the reagent, or to sell it, to prepare it as two separate solutions that when mixed together in suitable proportions, give an effective Fischer reagent. The two solutions might be, for example, a solution of sulphur dioxide in pyridine and a solution of iodine in methanol.

A logical development of this practice was the use of Fischer reagent in the form of two solutions. This was proposed by Axel Johansson⁵ in 1947 and supported in a recent paper by Seaman, McComas and Allen.⁶ Johansson recommended that a mixture of pyridine, sulphur dioxide and methanol be used to dissolve or suspend the sample (Solution A) and that this be titrated with a solution of iodine in methanol (Solution B). The advantages of this procedure are that the iodine solution is reasonably stable, and therefore less costly to prepare, and that neither of the two solutions used is excessively hygroscopic, so that protection from the atmosphere is not so difficult. The reaction is said to proceed stoichiometrically according to the equation—



without side reactions, but because of the impossibility of preparing the two solutions from chemicals completely free from water it is necessary to standardise the iodine solution against water empirically. The stability of the iodine solution is borne out by figures quoted by Seaman⁶ and shown in Table I. The drop at the twenty-first day is accounted for by the fact that a drying tube fell off the stock bottle and was only replaced after a period not exceeding 15 hours.

TABLE I
PERMANENCE OF SOLUTION B

Time of standing, days	Effective water equivalence, mg of water per ml
0	1.985
3	1.966
7	1.953
14	1.952
21	1.937
28	1.907

For direct titrations this modification of the Fischer reagent merits consideration, but if an indirect electrometric or visual end-point is to be used, certain difficulties arise. When the normal Fischer reagent is prepared, a proportion of the iodine added is ineffective because it is used up in side reactions within the reagent. If in titrating with the modified reagent, an excess of iodine is added, a situation arises similar to that existing in freshly prepared normal Fischer reagent; some of the excess of iodine may be used up in side reactions and the result be erroneous. From a study of this problem, Seaman concluded that a satisfactory determination could be made, by means of the dead-stop end-point if necessary, provided that the test solution was cooled to -10° to -15° C, not more than 10 ml of excess iodine reagent was added and the mixture was not allowed to stand for more than 10 minutes prior to the back titration.

The only new development in the standardisation of normal Fischer reagent that is worth mention is standardisation with sodium acetate trihydrate, which is more convenient to handle than water, but does not yet appear to be in widespread use.

METHOD OF TITRATION AND DETERMINATION OF THE END-POINT

The simplest method of titration with the Fischer reagent, provided that neither the reagent nor the solution being titrated are unnecessarily exposed to the atmosphere, is a direct titration to a visual end-point. This requires only a little practice in judgment and, for this purpose, Smith and Mitchell¹ have advocated the use of two standard colours, one the colour of the iodine end-point and the other the colour of the "spent" reagent just before the end-point. Such standards are readily prepared, but a more formal arbitrary standard has been suggested by G. K. Jones⁷ who recommends the use of N/300 iodine solution, and although Smith and Mitchell spurn this idea, in the revised specification for hexachloroethane the British Standards Institution have adopted a control end-point solution of N/200 iodine to assist judgment of the end-point of a Fischer titration.

When the material to be examined is coloured, or when increased accuracy is required, an electrometric end-point may be used. The first titration that employed such an end-point was reported by Almy, Griffin and Wilcox,⁴ who were titrating back an excess of Fischer reagent with a water solution. They found that if two electrodes, one platinum and one

tungsten, were placed in the test liquid, a small but definite change in potential occurred during the final discharge of the iodine colour by a standard water-in-methanol reagent, the tungsten becoming more positive with respect to platinum. This method has proved satisfactory in practice, but for routine use it suffers from the two disadvantages that (a) a suitable potentiometer or pH meter is required and (b) the tungsten electrode must be cleaned whenever it becomes tarnished; this is done by dipping it into molten sodium nitrite.

The dead-stop end-point technique has neither of these disadvantages. The principle was first described by Foulk and Bawden⁸ in 1926 and it was first used in a Fischer titration by Wernimont and Hopkinson⁹ in 1943. This back titration technique has become very popular; deservedly so, because only a very simple circuit is required, as can be seen in Fig. 1, and it can, therefore, be built in any laboratory and used with confidence by

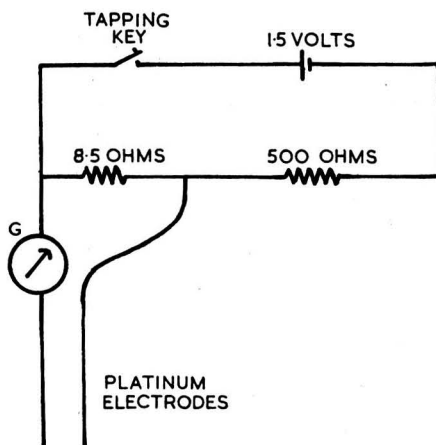


Fig. 1. Circuit for dead-stop end-point

laboratory assistants. Because the Fischer reagent is so hygroscopic it is now quite common for apparatus assemblies to be designed for performing a titration in which the test liquid is completely isolated from the atmosphere. It is usual for the dead-stop end-point circuit to be included in such assemblies and stirring of the liquid is often done magnetically. A number of such pieces of apparatus have been described in the literature and it is now possible to buy one from a laboratory supply house. A typical set-up¹⁰ is shown in Fig. 2.

McKinney and Hall¹¹ suggest that the galvanometer should be replaced by a "magic eye" cathode ray tube and its associated circuit. Suitable apparatus is available commercially both in this country and in America.

Most investigations of electrometric systems have involved back titration in the belief that more accurate and precise results could be so obtained. The normal dead-stop end-point has been found to be less sensitive in the forward direction, but several direct titration procedures have been proposed and appear to be of good accuracy. An example of this method is that of Carter and Williamson,¹² who used the circuit shown in Fig. 3. The platinum electrodes were connected in series with a 2-volt cell, a high resistance, tapping key and a sensitive galvanometer. The galvanometer was shunted by a resistance between 1/40th and 1/10th of that of the galvanometer itself. The resistances shown in the figure were those used by Carter and Williamson as being the most suitable for their particular apparatus. The e.m.f. applied to the electrodes varied during the titration since the resistance of the electrode solution system decreased from an initial value of greater than 15,000 ohms to approximately 500 ohms at the end-point. In methanol solution the potential varied from 1 to 2 volts at the beginning of the titration to about 0.15 volt when the titration was completed. The titration was carried out in the usual type of cell protected from the atmosphere. At the beginning, the reagent was added rapidly to the stirred solution in 0.2-ml portions. The galvanometer deflection was fairly constant until the end-point was approached, when small oscillations began to occur. The reagent was then added dropwise, and when the end-point was reached, a surge of current was produced and the galvanometer was deflected about 50 mm to a new steady value. Thus no readings of current or resistance were necessary to obtain the end-point, the galvanometer being so adjusted that, although

the spot might be off the scale for the early part of the titration, it moved on to the scale in time for the final surge of current to be observed.

In these direct titrations there is no need for a burette holding standard water-in-methanol solution, and this makes for simplicity. From the published data the end-point appears to be as sensitive and as accurately reproducible as that of indirect procedures.

Within the subject of end-points comes the use of micro-titrations, a development which may find widespread application. Mitchell and his co-workers¹ found that a reagent

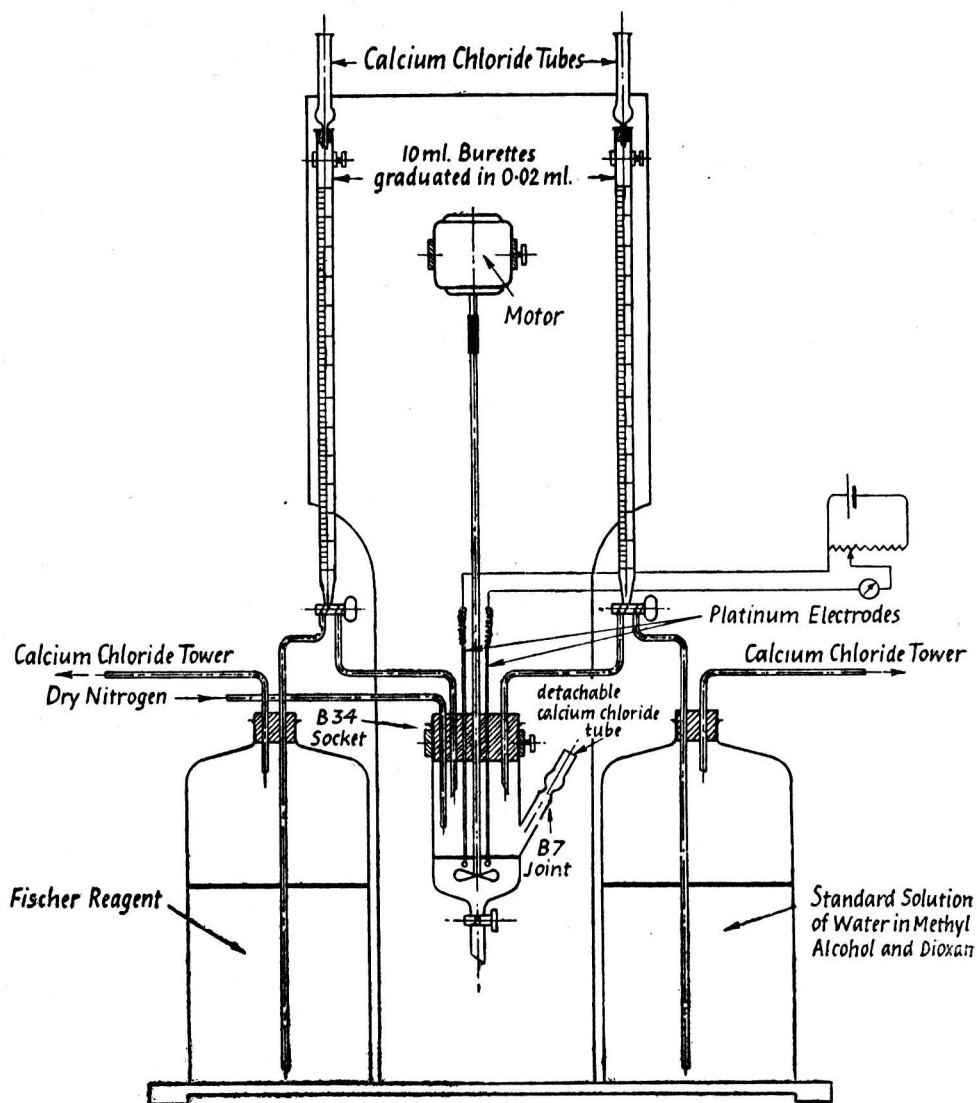


Fig. 2

having a water equivalent of 1 mg per ml could be used satisfactorily to obtain a visual end-point, but with reagents of a lower water equivalent than this the visual end-point could not be reproduced with sufficient precision to be practical. It is probably that the electrometric end-point is more suitable for micro-work than the visual one, and a useful development in this field has been the design by Levy, Murtaugh and Rosenblatt¹³ of the novel micro-titration assembly shown in Fig. 4. Precautions must be taken to ensure protection of the titration from the atmosphere, especially during the preliminary preparation, but when these are taken, very high accuracy and precision can be claimed for the technique.

THE VERSATILITY OF THE FISCHER METHOD

The Fischer reagent is extraordinarily versatile. As mentioned earlier, it has been used for determining the water of hydration of salts of organic acids such as sodium acetate or sodium succinate. Hydrates of the salts of inorganic acids have also been analysed successfully. Many hydrates of high stability are attacked rapidly by the reagent, and relatively insoluble hydrates, for example, cobalt sulphate ($7\text{H}_2\text{O}$) and magnesium sulphate ($7\text{H}_2\text{O}$),¹

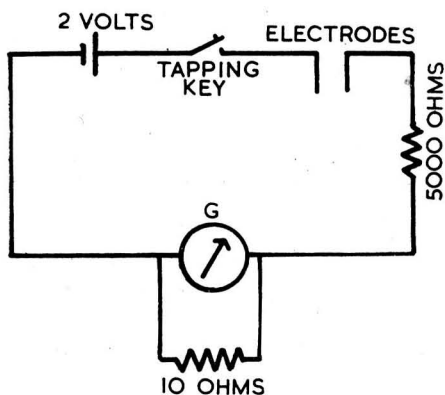


Fig. 3. Carter and Williamson circuit

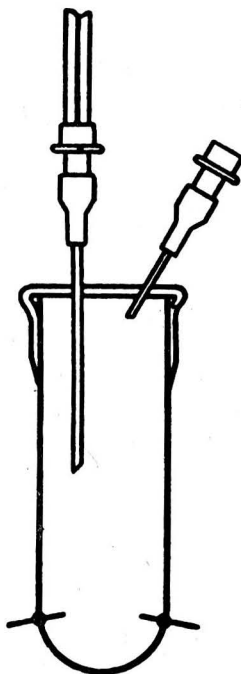


Fig. 4. Titration cell for use with Karl Fischer and standard water reagents supplied through hypodermic needles inserted through a self-sealing rubber cap

are often dehydrated completely, provided that the samples are finely ground and the mixtures shaken mechanically with excess of reagent.

Although not many inorganic acidic compounds have been investigated, the method has been applied successfully to hydrogen chloride,¹⁴ hydrogen fluoride¹⁵ and liquid sulphur dioxide.¹⁶

In attempting to apply the method to many inorganic compounds, interference from side reactions is often encountered and consequently it is essential to have a knowledge of the nature and stoichiometry of these interfering reactions for the reagent to be used successfully.¹ For example, the determination of water in zinc oxide or similar oxides would have to take into account the fact that oxides react with the hydriodic acid present in small amounts in Fischer reagent, even when buffered with pyridine, as in the equation—

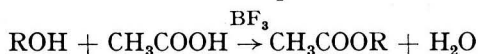


This water reacts with the reagent and the net effect can be expressed by the equation—



Another application of the Fischer reagent is to the quantitative determination of organic functional groups through organic reactions involving the liberation or consumption of water. Functional groups that have been determined in this way include alcoholic hydroxyl, organic carboxylic acids, acid anhydrides, carbonyl compounds, amines, nitriles and peroxides. Almost the whole of the work required to develop these applications appears to have been done by Mitchell and Smith and their co-workers, and a detailed account has been given for the first time in their recently published book.¹ There is space for a very brief discussion

of only one of them. It had been found by Nieuwland and his co-workers¹⁷ in the early 1930's that boron trifluoride was an effective esterification catalyst. This was made the basis of a new volumetric procedure for alcoholic hydroxyl, independent of acidimetry, when Bryant, Mitchell and Smith¹⁸ found that by employing a large excess of acetic acid with boron trifluoride as catalyst the acid-ester equilibrium could be shifted almost completely in favour of water and ester as shown in the equation—



The water formed, which was equivalent to the hydroxyl, was determined by direct titration with Fischer reagent after pyridine had been added to destroy the effectiveness of the catalyst. This procedure was found to be applicable to all types of primary, secondary and tertiary aliphatic and alicyclic alcohols as well as such aromatic alcohols as had the hydroxyl group attached to an aliphatic side-chain. Except for phenols, which did not react completely, the method was applicable over a wide range of compositions and was remarkably precise in the presence of large amounts of water, acids or easily hydrolysed esters.

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DISCUSSION

DR. W. ROMAN opened the discussion, and subsequently contributed his remarks in the form of the following Note—

THE APPLICATION OF THE FISCHER REAGENT TO THE DETERMINATION OF MOISTURE IN GASES

Mr. Jones has given a comprehensive survey of the application of the Fischer reagent to many problems. I want to add to this a new application which occurred to us. It is possible to determine moisture in gases by passing the gas directly into Fischer reagent in a special cell as shown diagrammatically in Fig. 2 and by employing the dead-stop end-point method which has been described already by Mr. Jones in his paper.

The gas is bubbled through the Fischer reagent, entering through a fine jet which allows single bubbles to come up through the solution when a slow gas flow of about 1 litre per minute or less is employed. Fig. 1 gives the circuit employed by us, which is very similar to those used by other applications of the Fischer reagent. The passage of gas through the reagent results in some methanol being evaporated, particularly inside the jet, so the Fischer reagent used is more dilute than that normally employed. No other solvent is employed. The cell is filled with a few millilitres of Fischer reagent, which absorbs all moisture inside the cell and thereby ensures complete freedom from any extraneous moisture. Gas flows through the three-way tap to waste until the lines (see Fig. 2) are sufficiently purged to remove any moisture in them. Then, by turning the tap, the gas is allowed to pass through the cell until the galvanometer needle drops to zero, at which point the gas supply to the cell is cut off by turning the three-way tap to waste. The reagent in the cell is then in a deadened state, and a completely dry solvent is ensured. Fresh Fischer reagent is added from the burette, connected directly

to the cell. With a 5-ml micro-burette, as little as 0.01 ml can be added at a time. This small amount is distributed sufficiently in the liquid by the gas stream itself, and the galvanometer needle registers immediately. Gas is allowed to flow through the cell and out through a drying tube and through a gas meter until the galvanometer needle has again dropped to zero. The amount of gas passed is recorded and the amount of water in this amount of gas is given by the water equivalent of the Fischer

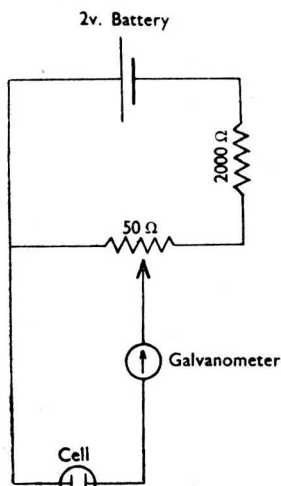


Fig. 1

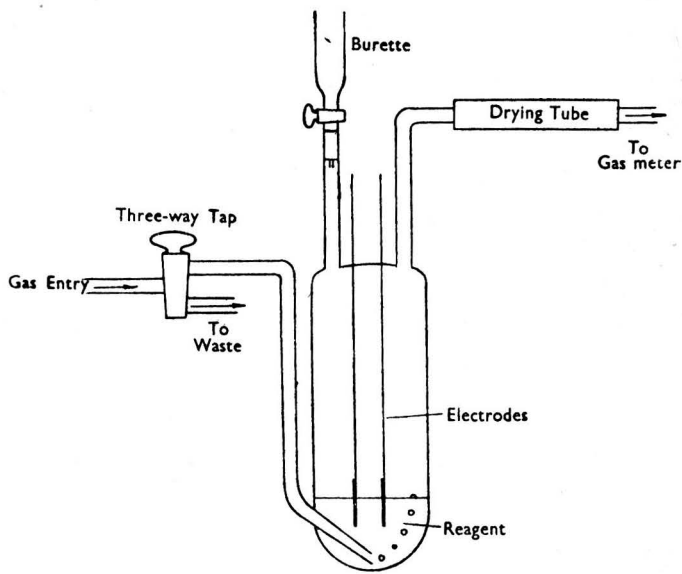


Fig. 2

reagent added. The drying tube at the cell outlet prevents any back diffusion of moisture into the cell.

The method has been employed, with air, nitrogen and hydrocarbon gases. It is suitable for ethylene and propylene; higher olefines have not been examined. With the slow rate of flow specified, all of the water was absorbed in the few millilitres of solution used. The method is only used for fairly dry gas, and can determine as little as 20 μg of water per litre.

W. ROMAN
A. HIRST

MR. ALFRED WRIGHT then asked Mr. Jones whether the reagent could be used in the presence of unsaturated bodies capable of reacting with the iodine, in view of the inaccuracies occasionally experienced by the questioner when determining moisture in bleached shellac. Had the author had any experience of this matter?

MR. JONES replied that he had had no experience of this, but obviously the reagent could not be used where the material examined reacted with the reagent unless some steps were taken to prevent such interference.

DR. H. J. CALLOW said that, as far as he was aware, the reagent could not be used for determining the moisture in textile fibres because of the presence of organic functional groups, *e.g.*, amino and phenolic groups in protein fibres, alcoholic groups in cellulose, and alcoholic as well as phenolic groups in the bast fibres. Organic groups of this type were known to react with the Karl Fischer reagent and thus it was doubtful if the method could be used for moisture determination in these products.

MR. L. G. BECKETT said that it was apparent from the paper and subsequent discussion that, admirable as the Karl Fischer method was, it could give misleading results especially when estimating the moisture content of many biological materials, and under some conditions could result in the denaturation and destruction of the material being examined, *e.g.*, bacterial cultures and virus suspensions. In his laboratory a non-destructive physical method of moisture determination had been developed.

Water was removed under high vacuum and condensed on a cold surface within the vacuum system. After a predetermined time the specimen was isolated from the system, the refrigerant was removed from the cold trap and the condensed ice thereon was allowed to evaporate. From the increase in pressure within the system as a consequence of this evaporation, the known volume of the system and the air temperature, the mass of water condensed could be calculated. By this method the rate of loss of water could be determined under experimental conditions similar to those existing during processing on a macro-scale.

It should be possible to differentiate between the removal of chemically bound moisture. Moisture determinations between 10^{-4} and 10^{-7} g could easily be made with simple, robust apparatus.

Mr. J. HASLAM asked if Mr. Jones had any experience of the application of the principles of the Karl Fischer reagent to the determination of water in sodium hydroxide.

Mr. JONES replied that he had not attempted such a determination. This did not appear to be of particular interest to manufacturers of sodium hydroxide and so had received little attention, but the little work that had been done was described in Mitchell and Smith's book.

Mr. K. EBBUTT said that the author had drawn attention to the fact that some inorganic compounds, such as zinc oxide, react with the Karl Fischer reagent. Mitchell and Smith indicated that many of these side reactions are stoichiometric and that a correction can therefore be applied. With oxides, carbonates and so on containing relatively large amounts of moisture, this correction would introduce very large errors. Had Mr. Jones any experience of the use of organic solvents for extracting moisture from such substances, followed by titration of the solvent, and could he say whether the method was satisfactory?

Mr. JONES replied that it was quite a common procedure to extract a sample with, say, methanol or to distil off the water as an azeotrope with some suitable solvent.

Mr. D. M. FREELAND asked if the Fischer reagent was useful for the determination of moisture in various materials such as glycerol and sugar syrups, and whether any sulphur dioxide used as a preservative in a glucose syrup would interfere with the reagent. Would there be any chance of side reactions owing to the presence of many hydroxyl groups in such materials?

Mr. JONES replied that such materials had been examined satisfactorily by this method. It was unlikely that sulphur dioxide would interfere.

A Radio-Frequency Electronic Moisture Meter

By A. T. S. BABB

(Presented at the meeting of the Society on Wednesday, February 1st, 1950)

A moisture meter based on change of permittivity with moisture content and utilising radio frequencies is described. Examples are given of its use for the examination of materials of widely differing texture and moisture content. The meter is shown to be accurate within 0.3 per cent. of moisture over its whole working range, which is from 1 or 2 per cent. to 60 per cent. of moisture, provided that measurements are made under the same conditions as are used for calibration.

CONDUCTANCE and permittivity are properties of a substance which, as a rule, are greatly influenced by the moisture content, and many electronic meters have been designed to measure one or both of these properties and hence to indicate the moisture content of the material under examination.

Meters based on the measurement of conductance are simpler than those designed to measure permittivity or capacitance, but the range of moisture content over which they are sensitive is usually limited. The conductance of the material is largely due to the solution of ionisable compounds. In many materials of low moisture content the water exists to a very great extent as "bound" water, and in these materials, for a small change of moisture content, the change of conductance is too small to be measured. When the moisture content is high, ionisation may be complete, and then a conductance meter may be insensitive to change of moisture content. A further objection is that for the accurate measurement of conductance the conditions of contact of the material with the electrodes must be reproducible, a requirement not easily satisfied if the texture of the material to be examined varies with moisture content or if it is not a homogeneous product. The conductance method could not, for example, be employed for the examination of lumpy or coarsely-chopped materials, particularly if the sample must be large in order to obtain a result that is representative of the bulk.

Meters that depend on change of permittivity and that measure capacitance can be made to indicate moisture content because the permittivity of water is 81 while that of most dry materials lies in the range 2 to 4. Provided, therefore, that the water is not combined, chemically or physically, with any other constituent of the material, permittivity should increase steadily with moisture content; but the contribution to permittivity of "bound" water is very much less than that of "free" water, and for any material in which some of the

water is "bound" it would be expected that, as the moisture content is increased gradually from zero, the permittivity would increase slowly at first when the added water becomes nearly all "bound," but more rapidly as the proportion of the added water that becomes "bound" progressively decreases. This has been found to be so in practice. A meter for measuring capacitance should therefore be so designed that its sensitivity to change of moisture content increases as the moisture content decreases.

Meters based on measurement of permittivity or capacitance are of two general types, those that employ low frequencies of the order of 50 to 5000 c/s and those using radio frequencies of upwards of 100 Kc/s (the meter described in this paper utilises a frequency of 10 Mc/s). Low frequency meters are usually insensitive at low moisture contents because of the difficulty of measuring small changes of capacitance with the impedance bridge circuits they usually employ, and at high moisture contents the ohmic resistance of the sample may be affected by texture. A change of ohmic resistance that would have little or no effect on the response of a meter employing a high frequency could introduce serious errors in one operating at a low frequency.

There are several radio-frequency moisture meters on the American market but, as far as is known, the only meter available in this country was designed specifically for the examination of textiles. The meter described in this paper was designed for the examination of a very wide range of materials with moisture contents as low as 1 or 2 per cent. or as high as 60 per cent., for powdered, granular or coarsely chopped products and for materials in the form of sheets, shaped pieces or wrapped packets. It was considered that a meter of such great versatility should find many applications, but it was also realised that, as distinct from an "all-purpose" meter, the need would arise in specific cases for a meter that would provide maximum sensitivity over a particular but limited moisture range. The instrument was designed with the following points in mind—

- (i) The provision of sample cells of varying dimensions to cater for materials of widely differing character.
- (ii) The ability to suit the dimensions of the sample cell to those of the articles to be tested in special cases.
- (iii) An electronic circuit that would be sufficiently sensitive to small changes of permittivity over a wide range of permittivity.
- (iv) An electronic circuit whose sensitivity to change of permittivity would be greatest when the permittivity was least.
- (v) An electronic circuit that, by the mere alteration of the values of some of its components, could, in a given instance, be made to operate with great sensitivity over any required, limited, moisture range.

The "all-purpose" meter employs a frequency of about 10 Mc/s and operates with materials which have an effective permittivity between 1 and 20 and which increase the capacitance of the sample cell by 0 to 25 $\mu\mu\text{F}$. Only a brief description of its essential features need be given in this paper.*

THE ELECTRONIC CIRCUIT

The circuit is shown in Fig. 1. Apart from the power pack it comprises three essential sections—

- (i) *The cell oscillator*, which generates a signal whose frequency is governed solely by the capacitance of the tuned circuit.
- (ii) *The frequency changer*, which receives the signal from the cell oscillator and generates another signal whose frequency is governed solely by the frequency of the signal received.
- (iii) *The indicator*, which receives the signal from the frequency changer but which gives a visual response only if that signal has a single, pre-arranged frequency. It gives a visual indication when—and only when—the frequency of the original signal generated by the cell oscillator has a pre-arranged value, *i.e.*, when the tuned circuit of the cell oscillator has a pre-arranged capacitance.

* It is intended to publish a more technical description of the circuit elsewhere. The meter has been named "The Kappa Moisture Meter" (Prov. Pat. No. 124752/47) and both the "all purpose" meter and meters for special applications are manufactured under licence by Messrs. Toplis Simpson and Co., Ltd.

THE CELL OSCILLATOR—

Only the method of control of capacitance need be described. One component of this circuit is the sample cell, or condenser C2; when the capacitance of this condenser is increased, as when a sample is put into the cell, the capacitance of the tuned circuit is increased and the frequency of the generated signal is reduced. If the capacitance of the circuit be now gradually

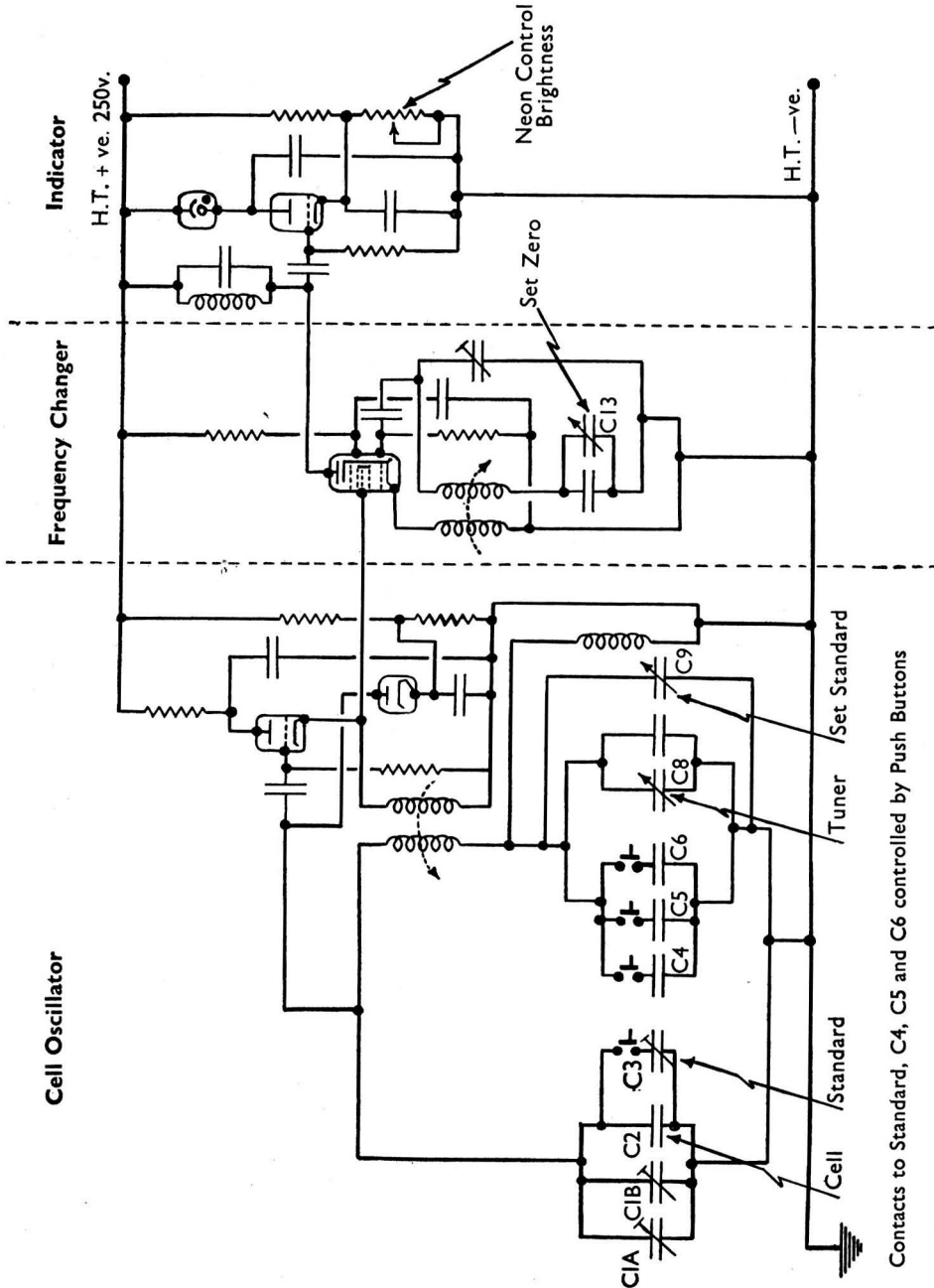


Fig. 1. Circuit diagram

reduced by the adjustment of a condenser, say the condenser C1A in parallel with the cell, the capacitance of the circuit will eventually reach its former value and the signal will have its former frequency. Thus, provided the meter had first been tuned to that frequency,

the indicator would show that the capacitance added by way of the sample had been exactly nullified by the adjustment of C1A, and this adjustment would therefore be a measure of the capacitance of the sample. Such a method could not be adopted in practice because the added capacitance is small, and its variation with moisture content is so small that changes of the order of $0.01 \mu\mu\text{F}$ would have to be detected by the use of a very fragile and insufficiently stable component. Removal of capacitance by the operation of series condensers instead of parallel condensers has therefore been adopted and the design is such that the ratio of capacitance to be removed to capacitance added by way of the sample is at least 50 when the latter is $1 \mu\mu\text{F}$ and 12 when the latter has the maximum value of $25 \mu\mu\text{F}$ for which the meter provides. The removal is effected partly by the operation of the tuning condenser C8 which has a working range of $60 \mu\mu\text{F}$ and is ganged to a pointer which moves over a scale, and partly by a series of condensers, C4, C5 and C6, which by the operation of push-buttons remove capacitances in five increments each of $50 \mu\mu\text{F}$. The push-button unit therefore functions as a range-selector switch so that, of the total capacitance to be removed, not more than $60 \mu\mu\text{F}$ is recorded on the scale, which is marked linearly with well-spaced graduations. The design of the circuit thus combines a very large magnification of the capacitance of the sample with an easily read scale.

Two controls of this circuit are provided—the Standard control C3, operated by push-button, and the Set Standard control C9; in conjunction with the control C13, a component of the frequency changer, they are used to align the meter before use. By their adjustment the indicator is made to respond visually when the sample cell is empty and again when a standard capacity is introduced in parallel with the cell and a pre-arranged capacitance is removed by operation of the push-buttons and tuner. In this condition the meter operates correctly over its whole working range.

THE FREQUENCY CHANGER—

The frequency changer section contains two parts, a control oscillator of the same type as the cell oscillator and a signal mixer. The oscillator generates a signal of fixed frequency, about 10 Mc/s (adjustable for alignment purposes by the Set Zero control C13). During the operation of the meter this signal, called the control frequency, is continuously fed to the mixer which also receives the signal from the cell oscillator. These two signals are electronically "mixed," and the mixer is caused to generate a third signal whose frequency is equal to the difference between the frequencies of the two signals received. The third signal is passed to the last section of the meter, the indicator. The control frequency is made slightly greater than that generated by the cell oscillator when the cell is empty, so that a relatively small change of the cell oscillator frequency induces a relatively large change of the frequency of the third signal. For example, the "all-purpose" meter is designed to have a control frequency of 10.000 Mc/s and a cell oscillator frequency (cell empty) of 9.630 Mc/s; the third signal therefore has a frequency of 0.370 Mc/s, to which frequency the indicator is designed to respond. If the frequency of the cell oscillator decreases to 9.620 Mc/s, a change of 1 in 963, the frequency of the third signal increases to 0.380 Mc/s, a change of 1 in 37. In this way the sensitivity of the meter to change of frequency of the cell oscillator is magnified 24 times.

THE INDICATOR—

The indicator is designed to respond to a signal of fixed frequency (0.370 Mc/s in the "all-purpose" model) and only if the third signal has this frequency does the neon lamp respond. In practice the frequency band over which the indicator operates is about 0.02 Mc/s, from 0.360 to 0.380 Mc/s, and the peak intensity of illumination can be judged to within 0.002 Mc/s. Thus the indicator shows that the frequency of the third signal lies between 0.368 and 0.372 Mc/s and therefore that the frequency of the cell oscillator signal lies between 9.632 and 9.628 Mc/s.

The meter is therefore extremely sensitive to change of frequency. It has not been found necessary to provide any stabilising circuits; this is because the cell and control oscillators are of the same type and, although mains fluctuation or temperature change might cause frequency drift, any drift would be common to each oscillator and the frequency difference (the third signal) would be unaffected.

SAMPLE CELLS

To enable materials of widely different texture to be placed in the cell in a standardised manner, and for convenience and cleanliness, the sample is not put directly into the meter but into a container, made of Perspex, that slides smoothly into position between the plates of the condenser C2. According to the nature of the material, one of three sets of cells and containers should be chosen. The small container holds 100 to 200 g of material (depending on its bulk density) and is designed for use with powdered or finely granular material. The medium-sized container holds 400 to 800 g, and is for coarse granules, pellets, tea, material in sheet form, biscuits, small tablets and similar articles. The large container is intended for larger irregularly shaped pieces, or for use when a very large sample must be taken to be representative of the bulk; this container holds 1000 to 2000 g.

The small container is provided with a compression block fitted with an adjustable stop so that, for materials of variable bulk density, the volume as well as the weight of the sample can, if necessary, be controlled. Within certain limits, cells and containers can be designed to suit the dimensions of shaped articles or packaged goods and to fit into the standard meter.

OPERATION

The meter having been aligned, the testing of a sample is performed as follows—

A pre-arranged, convenient weight of sample is taken; weighing must be accurate to ± 0.5 per cent., or to ± 0.2 per cent. if the moisture content is low and the greatest accuracy is required. The sample is transferred to the container in a standardised manner and compressed if necessary. The container is placed in the meter and the push-button and tuner set to give a peak intensity of the indicating light. The position of the pointer on the scale card is recorded. The temperature of the sample is taken and the scale reading corrected for temperature if necessary. The moisture content is read from a calibration curve, or directly from the scale card if this has been graduated for the material under test.

Tuning the meter to the peak intensity takes about one minute if all the moisture ranges have to be searched, but only a few seconds in routine work when the approximate moisture content is known.

CALIBRATION—

The meter measures indirectly the change of the capacitance of the condenser C2. This change is governed by the permittivity of the dielectric, *i.e.*, the sample under test, but whilst the permittivity of the sample generally increases with moisture content there is no simple relationship that enables one value to be expressed in terms of the other. Therefore, in common with all electronic moisture meters, the meter here described must be calibrated for use with the particular material that it is required to examine.

The meter is calibrated by taking three or more readings for each of a sufficient number of samples of known but different moisture contents so that a calibration curve to cover the required moisture range may be drawn.

The sets of three or more readings show the degree of reproducibility of results and give an indication of the accuracy to be expected. The temperature correction is obtained by calibrating with the samples at two or three different temperatures.

It will be appreciated that the routine followed in the subsequent determinations must be the same in all details as that adopted for the calibration.

The scale card may be calibrated directly in terms of moisture content from the calibration curve.

PERMITTIVITY AND MOISTURE CONTENT

The permittivity of the material depends mainly on its moisture content, but also on a number of other factors the most important of which are—

- (a) The proportion of the total moisture that is "bound" or chemically combined with the material.
- (b) The composition of the dry material.
- (c) The bulk density of the sample.
- (d) The disposition of the sample particles or pieces with respect to the condenser plates and to each other.
- (e) The temperature of the sample.

It follows that unless these factors are constant, or change steadily with change of moisture content, the meter cannot give reliable results. It also follows that for any one material the method of filling the container must be standardised in such a way that "packing errors" are minimised. In this respect no difficulty is experienced with materials of uniform particle size unless texture varies largely with moisture content. With irregularly shaped pieces "packing errors" can be sufficiently reduced by taking large samples, and uniformly shaped articles should be packed in pre-arranged and regular formation.

APPLICATIONS

Without experience with similar materials it is impossible, in a particular example, to predict either the accuracy with which moisture content could be determined or the sensitivity of the meter to change of moisture content. This is because of the widely differing properties of materials—texture, composition, grain-structure, water-combining powers, etc.—and trial alone will show whether the meter can usefully be applied to the examination of a particular material. Some typical examples of the use to which the meter has so far been put are shown graphically in Fig. 2. The curves illustrate, for a great variety of materials and moisture

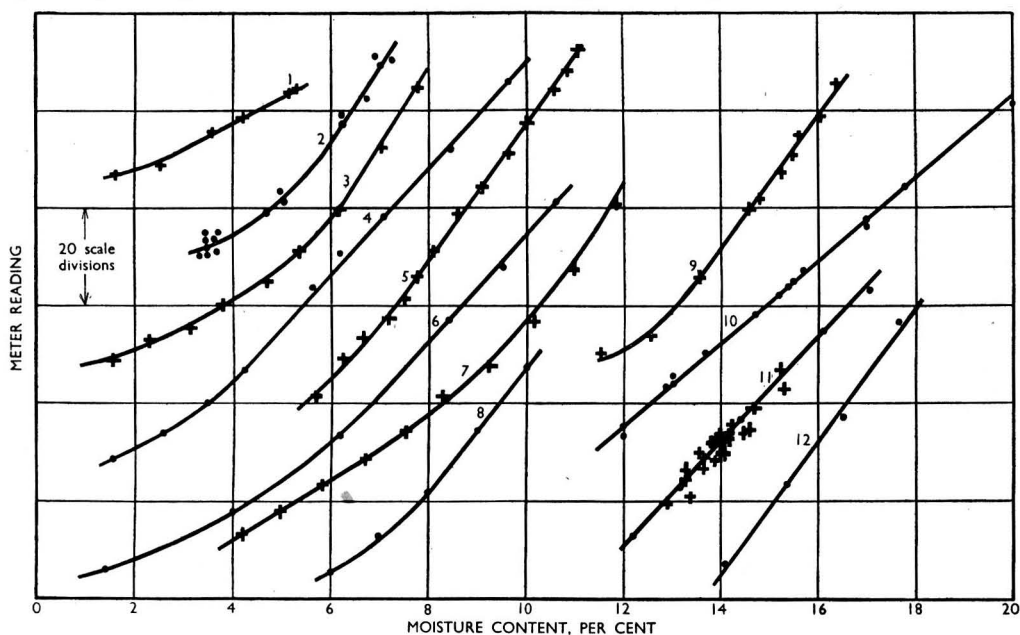


Fig. 2. Relationship between meter reading and moisture content. Curves for—

- | | |
|--|--|
| (1) Biscuits | (7) Tea |
| (2) Spray-dried whole egg (several different brands) | (8) Fish meal |
| (3) Dried ground chicory | (9) Powdered gelatin |
| (4) Sulphamerazine granules | (10) Rye grain |
| (5) Cops of cotton | (11) Flour of one type only —●—●— |
| (6) Cornflakes | (11) Flour of several types, strong, weak, chlorinated, etc. —+—+— |
| | (12) Dried chicory roots, sliced |

ranges, that the meter is adequately sensitive to change of moisture content. As an example of a substance with a moisture content greater than 20 per cent., alumina granules gave a curve with an average slope of 7 scale divisions for 1 per cent. of moisture over the range 13 to 38 per cent. of moisture; determinations were made with an error not exceeding 0.3 per cent. of moisture over the whole range.

The author wishes to thank the Directors of Messrs. J. Lyons & Co., Ltd., for permission to publish.

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DISCUSSION

DR. J. D. DERMOTT HARDING asked what was the effect of the temperature of the samples on the determination of moisture by the instrument described. Could the method be applied to inorganic substances, in particular to stable inorganic salt hydrates, such as aluminium fluoride?

MR. BABB replied that a small temperature correction to the apparent moisture content had in some cases been found necessary. Apart from alumina, with which good results had been obtained, inorganic substances had not as yet been examined.

DR. H. J. CALLOW asked whether the method could be applied to determine the average moisture content of a bulk sample such as a bale of jute which measured approximately 4 ft. \times 2 ft. \times 2 ft. and weighed about 400 lb.

MR. BABB said he thought it would be possible to design a cell for such a purpose provided there was no irregularity of shape. It might be found advisable to use a rather lower frequency with such a cell.

MR. R. L. STEPHENS said that in view of the small capacitance involved, the frequency should be increased and not decreased.

MR. BABB replied that the cell could be designed to keep the capacitance about the same as those met with in the normal cell. He had referred to the possibility of using a lower frequency, not to allow for a smaller capacitance, but to ensure that the wavelength would be many times greater than the dimensions of the cell.

DR. D. W. KENT-JONES asked what the meter actually measured when used for testing cereals that contained both free and combined moisture. Would a meter which made an accurate measurement of the natural moisture in grain also measure the moisture in a freshly damped sample?

DR. D. E. HAWKINS asked a similar question and stated that he had found electronic moisture meters unreliable for dried wheat, presumably because of uneven distribution of moisture in newly dried samples.

MR. BABB replied that he thought he had made it clear that the meter reading obtained was governed solely by the permittivity of the sample, and any property of the sample which affected permittivity—one such property being the distribution of moisture—would affect the meter reading. If the material was not in equilibrium with its moisture or could not be brought to the same condition as obtained when the calibration curve was constructed, an error would be introduced.

DR. PAGE asked whether any special packing precautions had to be taken for such materials as paper and biscuits. Would the technique apply to biscuits of different shape and texture?

MR. BABB replied that the sample must be placed in the cell in a reproducible manner. The results on paper had been obtained with sheets cut to a suitable size, and biscuits had been stacked in regular formation in the cell. Biscuits could be ground if that were convenient.

MR. H. T. SUTCLIFFE asked whether moisture could be accurately determined in a sample of soap chips taken directly from the drier and being dry on the outside and damp inside, and also in soap powder in which uncombined water is rapidly absorbed as water of crystallisation by sodium carbonate.

MR. BABB referred to his previous reply on the question of uneven distribution of moisture and said that in such instances only a trial, using samples taken under working conditions, would show whether the meter reading could be accurately related to moisture content.

The "Air Current" Method of Moisture Determination

With Particular Reference to Moisture in White Sugars

BY R. W. MONEY AND W. A. CHRISTIAN

(Presented at the meeting of the Society on Wednesday, February 1st, 1950)

For the routine determination of moisture in fine-grain white sugar, vacuum drying at 100° C was found to be inaccurate, the A.O.A.C. method, although valuable as the reference method, was too slow, and the Karl Fischer method was unsatisfactory owing to the need to maintain a supply of reagent, which deteriorates rapidly, for only three or four determinations per week.

Experiment showed that a method in which a preheated current of air was drawn through the sample in a specially designed apparatus gave satisfactory results. The apparatus and the method of operation are described and some typical results are tabulated to show their reproducibility. A comparison of results by the air-flow method with those by the A.O.A.C. and Karl Fischer methods showed satisfactory agreement.

THIS investigation arose from the necessity to determine moisture contents of about 0.05 to 0.3 per cent. in fine-grain white sugar (crystal caster) for use in a manufacturing process requiring freely flowing sugar particles. It was essential that the determination should be made rapidly, *i.e.*, in less than an hour, and should be accurate to within 5 per cent. The rapid method of drying a 1 to 2-g sample in a vacuum oven at 100° C was insufficiently accurate owing to the great significance of errors introduced by slight charring and by the normal experimental errors when such a small moisture content was being determined, while the A.O.A.C. method of drying to constant weight *in vacuo* at 70° C was too slow for routine purposes, although valuable as the reference method. Consideration was given to the Karl Fischer method and good results were obtained, but the method was not entirely satisfactory as it entailed the maintenance of a supply of reagent, which deteriorates rapidly, for the sake of three or four determinations a week. Various distillation methods were also considered but were unsuitable owing to the very small amount of moisture involved. It was thought that the rapid removal of moisture could best be effected by a current of warm dry air passed through the sugar in such a manner that all the particles were exposed to the air current and kept in motion by the air; the apparatus evolved and the results obtained by employing this principle are described below.

A preheated current of air has been used in many methods of moisture determination, but in only a few has the air been passed through the sample. In an oven method described by Spencer,¹ air is sucked over an electric heating element and through a metal capsule fitted with a metal filter cloth on which the sample is placed; drying periods of up to 20 minutes at 105° C were used for raw sugars. Meade² used the Spencer oven to determine the moisture content of molasses, syrups and honey by absorbing a dilution on asbestos, which was subsequently dried for a specified time; drying to constant weight was not recommended. Whittaker and Ross³ described an apparatus, the "Moisture Teller,"⁴ that was similar to the Spencer oven and consisted of a sample dish fitted with a 500-mesh screen as the bottom; the air stream was provided by a blower. The use of this apparatus for "roughages" was described by Monrose and Perkins.⁵ Since the method described in this paper was devised, Hardesty, Whittaker and Ross,⁶ and Ross and Love,⁷ have described an apparatus embodying crucibles fitted with sintered glass plates; they used this apparatus to determine the moisture content of fertilisers by heating at 60° C for two hours. In all these methods, the preheated current of air is drawn or blown through the sample in a downward direction so that loss of the finer particles is avoided, but tight packing may be aggravated and this would tend to lengthen the drying time. It was considered that the use of an upward current of air combined with precautions against the loss of fine particles would ensure that packing is minimised, that the particles are agitated and continually mixed, and that an even temperature would be attained.

THE APPARATUS

The general principle of the apparatus is shown in Fig. 1, in which the various parts are shown diagrammatically and unassembled. Standard ground glass joints were used. The sample container, S, is formed of two B29 cones fused together, and a sintered glass plate, P, of grade 3 porosity is fused into one cone. The sample container fits into the B29 socket of the heating unit, H, and is closed by the vacuum head, V, placed over the top cone. By the application of a vacuum at the outlet, O, air previously dried (by passage through silica

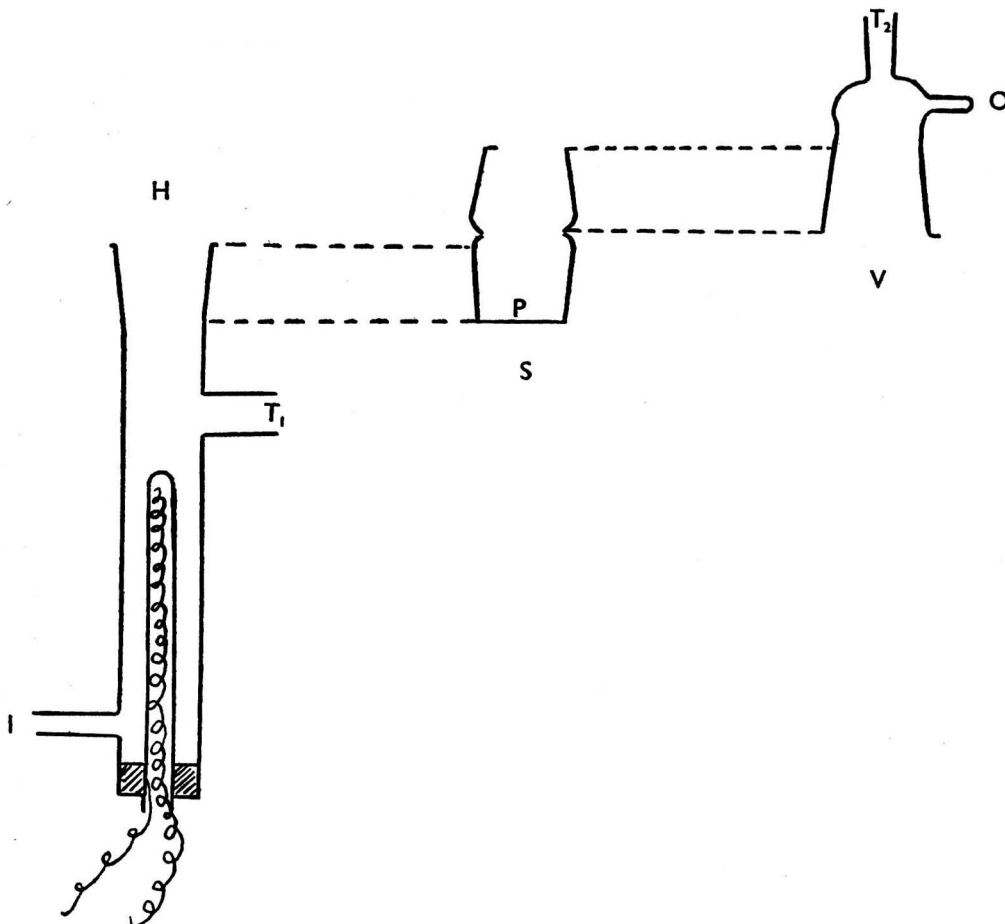


Fig. 1. Apparatus for air current moisture determination

gel, calcium chloride, sulphuric acid or other desiccant and filtered through cotton wool) is drawn in at I, round the heater, through the porous plate and the sample. Temperatures may be taken by the insertion of thermometers fitted with B14 cones into pockets T_1 and T_2 ; the temperature reached by the sample is referred to again below. Some care is necessary in the design of the heating unit to avoid the risk of volatilisation of metal or metallic oxide from the heating wire on to the porous plate, so causing an increase in weight. It is for this reason that the wire is enclosed in a sealed Pyrex tube, which serves to heat the incoming air. The heater current is obtained from a mains transformer tapped for 12 volts; the heater consumes 24 watts. The rate of air flow is controlled by the vacuum applied and is, of course, dependent on the porosity of the plate and tightness of packing of the drying towers, filter plugs, and so on. The flow should be just sufficient to keep the particles of the sample in motion without violent disturbance. In practice, the vacuum is gradually increased until the sample begins to "dance"; for caster sugar this occurs when the pressure in S (measured by a manometer connected to T_2) is reduced to about 36 cm of mercury. A

dry vacuum pump was used to produce the air current in this investigation; if a water pump must be used, suitable traps might be necessary to prevent water vapour passing back to the sample. In order to guard against the possibility of fine particles of the sample being carried away by the air current, a plug of cotton wool is inserted in the upper cone of S, and, as is shown below, provides an effective safeguard against the loss of even extremely fine particles.

METHOD OF OPERATION

The method of operation is as follows. A number of interchangeable containers, S, are fitted with cotton wool plugs, dried in the apparatus, cooled in a desiccator for 20 minutes and weighed, the procedure being repeated until constant weight is reached. The plug is removed, the sample of sugar, 6 to 8 g, introduced, the plug replaced and the weight found by difference. The sample container is then placed in the apparatus previously warmed by means of the heater, and air is passed for 30 minutes. The container is then removed, cooled in a desiccator for 20 minutes and reweighed. In general, for caster sugars, 30 minutes is sufficient time, but as a check, the container is replaced and air passed for a further 30 minutes.

During the preliminary work difficulty was experienced in that the moisture content of the sugar used as reference sample was neither constant nor uniform but changed with surprising rapidity with changing temperature, despite storage in a jar fitted with a screw cap and rubber washer. This was undoubtedly due to changes in the distribution of moisture over the surface of the sugar particles and could not be avoided by apparently thorough shaking. The effects were avoided by "conditioning" the sugar in a moist atmosphere (over 85 per cent. relative humidity) at 25° C for various periods of time, the sugar being spread out in very shallow layers and being well mixed at frequent intervals. The well mixed sample was then placed in small specimen tubes, each holding 7 or 8 g, which were completely filled with the sugar before being corked and waxed. The entire contents of a tube were then used for a determination.

TEMPERATURE OF THE SAMPLE

The temperature to which the sample was heated in relation to the temperature of the heated air before its passage through the porous plate was measured by modifying the apparatus to allow a thermometer bulb to be immersed in the 7-g sample of sugar in the container. The temperature of the air was measured by a thermometer placed in T_1 . The results are shown in Table I.

TABLE I

Duration of air flow, minutes	Temperature of sugar, ° C	Temperature of air at T_1 , ° C
1	24.5	80
2	29	92
3	36	101
6	50	110
9	57.5	111
12	61	112
15	64	112
18	65.2	112
21	66.2	112.5
24	67.0	112.5
27	67.3	112.5
30	67.7	112.5

These data showed that during the 30 minutes' heating period the temperature of the sugar did not exceed 70° C.

As in practice it would be highly inconvenient to have a thermometer immersed in the sample, a further set of temperatures was taken employing similar conditions of air flow and heating, but taking the temperature of the air above the sample, *i.e.*, by means of a thermometer inserted at T_2 . These results are shown in Table II.

Hence, to reach a sample temperature approaching but not exceeding 70° C, it is necessary to attain a temperature of 112° to 114° C below the porous plate (*i.e.*, at T_1), and one of 28° C above the sample (*i.e.*, at T_2).

POSSIBLE LOSS OF SAMPLE

In order to test whether or not fine particles of sugar might be carried away by the air current despite the cotton wool filter, some experiments were made with icing sugar, which contained about 10 per cent. of particles smaller than 270 mesh (0.053 mm) and so provided a much more severe test than the caster sugar, the particles of which were all greater than

TABLE II

Duration of air flow, minutes	Temperature above sugar at T ₂ , ° C	Temperature of air at T ₂ , ° C
1	20	93
2	21	102
3	21	106
6	23	111
9	24	112
12	25	113
15	26	114
18	26.5	114
21	27	114
24	27.5	114
27	28	114
30	28	114

100 mesh (0.147 mm). The apparatus was prepared as described above with the exception that the air after leaving the sample container was bubbled through a U-tube containing water. When the sugar had reached constant weight, no sucrose could be detected in the water by colour reactions sensitive to 1 mg. A second experiment was carried out in which five discs of Whatman No. 5 filter-paper were cut to fit the container above the cotton wool. These were dried and weighed and then placed in position over the container. When the icing sugar had reached constant weight, the discs were tested for the presence of sucrose by the method of Partridge and Westall.⁹ No sugar was found on any of the discs, although a similar disc on which 1 mg of sugar had been deposited gave a positive reaction. It was therefore concluded that the cotton wool plug was an effective safeguard against the loss of sugar.

TYPICAL RESULTS

The reproducibility of the results can be judged from the triplicate determinations of the moisture in three samples of sugar shown in Table III. The loss of relative precision when the moisture content is very small is due to the increased effects of experimental, sampling and distributional errors.

TABLE III

RESULTS OF TRIPPLICATE DETERMINATIONS OF MOISTURE IN SUGAR

Sample	Moisture			Mean	Spread, %
	(a) %	(b) %	(c) %		
A	0.445	0.437	0.440	0.441	±1
B	0.197	0.180	0.187	0.188	±4
C	0.055	0.059	0.062	0.059	±7

The moisture contents of ten samples of sugar are shown in Table IV, together with those obtained by drying to constant weight in a vacuum oven at 70° C. The moisture in four of the samples was also determined by the Karl Fischer method.

The agreement in general is satisfactory. Whether the observed differences are due to experimental error (in which must be included errors introduced by the uneven distribution of moisture in the samples taken), or to causes fundamental to the methods used, cannot be stated, but the good agreement between the results by the air current method and the chemically determined water of the Karl Fischer method would indicate that the vacuum oven method used was open to doubt for this type of determination. Although the A.O.A.C. method specifies an air vent to the oven, the flow of air is small and, as has been shown by Iles and Sharman,⁸ it is difficult to ensure a uniform air movement; moreover the sample of sugar on the bottom of a dish is virtually shielded from any air current.

TABLE IV
MOISTURE DETERMINATIONS BY DIFFERENT METHODS

Moisture by air current method, %	Moisture by drying at 70° C, %	Moisture by Karl Fischer method, %
0.415	0.399	0.420
0.171	0.165	0.174
0.166	0.161	—
0.164	0.164	—
0.121	0.120	—
0.103	0.110	—
0.065	0.075	0.067
0.064	0.081	—
0.061	0.052	0.058
0.060	0.080	—

Our thanks are due to the Directors of J. Lyons & Co., Ltd., in whose laboratories the work was carried out, for permission to publish, and to Dr. E. B. Hughes for his advice and interest.

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DISCUSSION

MR. H. POWERS said that there was a possible loss of dust from pulverised sugar, a small proportion of which may be as small as 10^{-5} inches. Some of the coarser conglomerates and grouping of crystals might not dry as soon as the separate particles.

MR. MONEY replied that the method was developed for the routine testing of caster sugar of specified particle size that excluded fine dust, but, as shown in the paper, no loss occurred even with icing sugar, all particles of which were less than 0.147 mm. No trouble has been experienced with conglomerates, which were normally absent from the sugar examined, but which have been produced artificially by damping the sugar and breaking up the lumps.

MR. ALFRED WRIGHT said that in a very similar method for resins it had been found that variations in particle size made very large differences to the results, even though resins were amorphous and not crystalline like sugar. Errors also arose from the tendency of the finely powdered portion of the sample to be blown away. As absolute uniformity of particle size was impossible without sieve grading and its consequent losses, and also since the method required the particle size to be very small for consistency of results and the small size of particle led to losses by blowing away, the method was considered to have too many inherent disadvantages and was discarded.

MR. A. L. BACHARACH suggested that figures for the reproducibility of the A.O.A.C. method, together with those reported by the author for his own, should make it possible to assess the significance of the occasional small differences that he found between them.

DR. K. A. WILLIAMS said that the principle described by the authors had been applied to other materials. In particular, he mentioned that in 1918 the Ministry of Food adopted as standard a method put forward by their Committee of Analysts for determining moisture in oils, and this was very similar to that now put forward.

It consisted in spreading the oil over a wad of asbestos contained in a tube and driving off moisture contained in the oil by means of a stream of dry inert gas at about 50° C. In the early form of the method the moisture removed from the oil was caught on calcium chloride or sulphuric acid and weighed. Later, however, it proved simpler to ascertain the loss of weight of the tube containing the oil on asbestos. Some care was necessary in choosing asbestos suitable for the test as some specimens had proved to lose moisture slowly and continuously when dry gas was aspirated over them, and these were clearly useless.

MR. R. A. FINCH said that Mr. Money had referred to the determination of moisture in dehydrated vegetables by his air flow method. It was well known that there was, as yet, no accurate means of measuring moisture other than by drying in vacuum for many hours. This was of no practical value where a large number of samples was being examined daily, and a method of drying dehydrated vegetables to constant weight in a short time, preferably in their unground form (dice or strip) would be very useful. He would be interested to know how long the author's method took, and what vegetable he had used.

MR. MONEY replied that he had tried tomato powder and potato powder. The amount of work done was very small, but drying did take some hours, and the indications were that the method was not as satisfactory as with sugar particles where the moisture was all on the surface.

MISS E. IRENE BEECHING asked the author whether he had used the method he described for the determination of moisture in high-boiled sweets, milk powders and chocolate crumb.

MR. MONEY replied that the method gave good results with chocolate crumb, but had not been tried for milk powders. Boiled sweets were effectively a glass, and the method could not be used unless the sample were pulverised, during which procedure it would probably absorb a certain amount of water, and even if it were possible to devise a method of pulverising the substance in absence of water, the result would probably depend on the particle size of the powder. Much work was needed on the determination of moisture in high-boiled sweets, before a satisfactory method could be devised.

MR. L. G. BECKETT drew attention to a statement in the paper that difficulty had been experienced in maintaining known moisture conditions in sugar retained in a Kilner jar closed by a rubber ring and screw-on cap. He said that it was not generally realised that rubber was permeable to water vapour. Considerable difficulty in this respect was experienced in the packaging of dried pharmaceutical preparations. Greaves¹ and Florsdorf² both referred to this permeation. It was possible that the variation in sugar moisture was due to water vapour flow through the diaphragm. Mr. Beckett asked whether the author had had any experience of back diffusion of water vapour from a water jet pump when used for aerating a sugar sample as described in the paper. He would not have expected back diffusion with the through-put of air necessary to maintain a pressure of 34 cm of mercury. In view of the long time necessary for completely drying sugar under vacua by the method described, had the author any experience of tumbling sugar under high vacuum conditions and the consequent effect upon the time required? Had Mr. Money considered equating his shorter drying time by air current methods to fundamental considerations of the kinetic theory of gases?

MR. MONEY replied that it was only a rubber washer, not a rubber diaphragm, that was used and therefore the joint was practically glass to glass. He agreed that back diffusion of water was extremely unlikely, but he preferred to take that precaution. The sugar was virtually tumbled but not at a very high vacuum and he had had no experience of the effects of tumbling under such conditions.

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The Determination of Moisture in Tobacco

BY C. F. M. FRYD AND P. R. KIFF

(Presented at the meeting of the Society on Wednesday, February 1st, 1950)

Moisture in tobacco is commonly determined by the statutory method as loss in weight on drying at a defined temperature. During recent years attention has been directed to the effect of variations in the time of drying and in the degree of ventilation in ovens; such variations, it has been shown, may seriously affect the apparent moisture content.

This sensitivity of the apparent moisture content to drying conditions is demonstrated to arise at least in part in a component which does not exist as moisture in the undried tobacco, but is produced by reactions of the Maillard type or by other reactions involving reducing sugar, during the process of drying.

Apparatus is described by the use of which experimental variations in the apparent moisture content of tobacco can be minimised.

For revenue purposes it is necessary to determine the moisture content of tobacco; and the relevant Acts of Parliament prescribe that this shall be taken as the decrease in weight when the tobacco is dried at a temperature of 212° by Fahrenheit's thermometer. As temperature is the only parameter mentioned, it is not surprising that until recently, interest was concentrated almost entirely upon it. Tate¹ drew attention to difficulties in the equalisation of temperature within ovens, and Fig. 1, reproduced from his paper, illustrates the extent of the variation that may take place in readings of the temperature at various points within an approximately cubical electrically heated oven. An internal fan rotating at sufficient speed was shown to obviate these variations, and a marked improvement in the repeatability of moisture determinations made in ovens so fitted was the result. Iles and Sharman² have recently described the effect of the rate of ventilation within ovens on the apparent moisture content of Bright Virginia tobacco. This type of tobacco has long been known to yield moisture results that vary with the apparatus in which the determination is made. Variations of this kind suggest that similarly discordant results may be expected in the moisture figures for other tobaccos and indeed for biological material in general.

As a sequel to the work of Iles and Sharman, which had been made available to us before publication, an oven was constructed in the Government Laboratory in which up to six 10-g samples of tobacco could be submitted for any desired time and at any pressure between fairly high vacuum and atmospheric to a metered ventilation. It was arranged that the apparatus could be totally and deeply immersed in a well-stirred glycerine-water bath, the temperature of which could be held to within 0.2° C at any point between 60° and 105° C (Fig. 2).

Preliminary experiments with this apparatus made it clear that the repeatability of moisture determinations (or more exactly loss-in-weight determinations) on cut tobacco was limited by the homogeneity of the samples.

For certain reasons interest in the Government Laboratory was directed especially to cigarette tobacco, and so the raw material for the experiments was obtained from a large number of cigarettes that had been submitted as samples.

Cigarette tobacco consists physically of finely shredded lamina of the leaf proper together with portions of the veins and midribs (known as stalk) contaminated with a small proportion of "sand," the residue of those particles of blown dust and soil which have not been detached during the process of manufacture. It is not difficult to mix this tobacco thoroughly; but in samples of 10 g (an amount frequently used for moisture determinations) variations in the proportion of stalk or sand from sample to sample of the mixed material still produces detectable variations in the apparent moisture. After several experiments, a technique to minimise these effects was devised. In a blender (Fig. 3) consisting of a closed drum some 56 cm in diameter and provided with some sixty inward-pointing 4-cm spikes attached to the inner periphery, the tobacco, in lots of about 1 kg, is tossed by rotation of the drum

for 24 hours at such a speed that the tobacco is just not carried round by centrifugal force but falls continuously from the highest point. (One end of the drum is made wholly of quarter-inch Perspex to facilitate the choice of the appropriate speed.) During this process the sand particles are shaken free and the shreds of tobacco are reduced in length more than are the portions of stalk and vein. The tobacco at this stage is removed and sieved, only the portion which passes 12 meshes to the inch and fails to pass 40 meshes to the inch being retained and returned to the blending drum for a further 30 minutes. After immediate removal at the expiry of this time, the tobacco is packed tightly into glass jars provided with

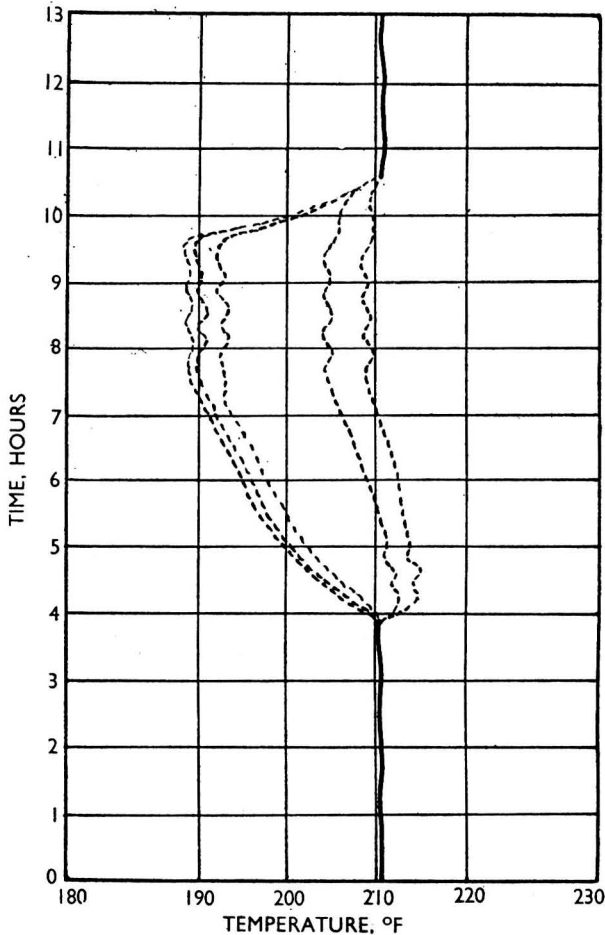


Fig. 1. Variation of temperature in electrically-heated oven

rubber sealing rings and holding some 200 g per jar. Experiments indicate that in these containers no noticeable alteration in apparent moisture takes place during storage of several months, as long as the containers themselves are stored in conditions of equable temperature.

For large-scale replicate work, the weighing out of samples requires the utmost care if loss or absorption of moisture by the sample is to be avoided. Two operators are needed, one of whom places in the previously tared and numbered drying-pan an approximate 10 g of the sample; the other weighs it immediately to the required (1 mg) accuracy on an aperiodic optical balance, and returns it to his companion, continuing with the next pan which has been prepared in the interim. The weighed pans are stored immediately in airtight containers, in order that the whole series of perhaps one hundred samples may enter the ovens in the same condition. Precautions must be taken to ensure that neither sunlight nor currents of air affect the moisture content of the bulk from which portions are being drawn; and all

portions removed from an overfull pan, or remaining in almost empty storage bottles, must be immediately discarded. With these precautions repeatability can be attained which for organic natural materials is of high standard (Table I).

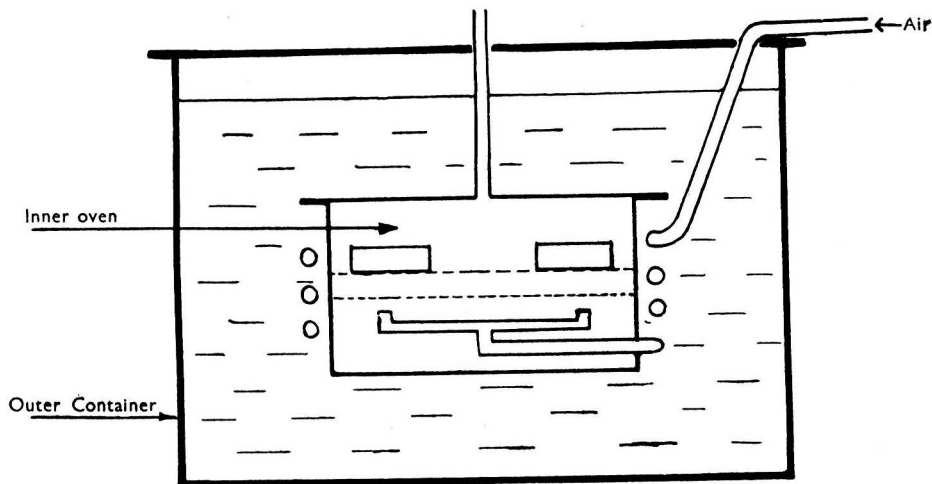


Fig. 2. Experimental oven

Table II shows the extent to which variations in the apparent moisture content can occur in homogenised material if the conditions of drying are artificially varied. Results of this nature called not only for the development of apparatus in which moisture determinations could be made under standard conditions, but also for some rational explanation of the cause of the discrepancies. Table III shows some results obtained in the Government Laboratory which illustrate the chemical effect of heating for various times and under varied

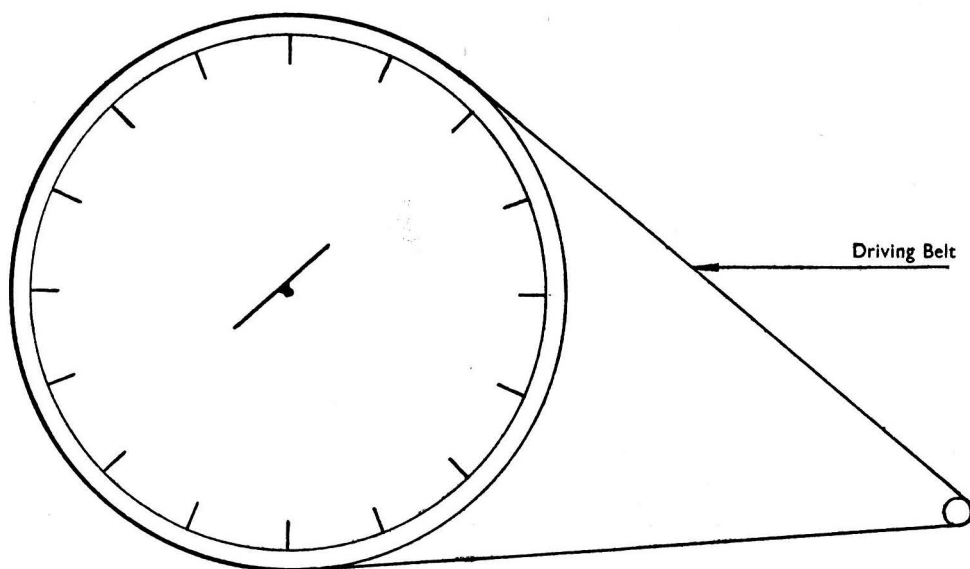


Fig. 3. Blender

conditions. It is immediately apparent that the major quantitative changes have taken place in the sugars present. Iles and Sharman² suggest that reactions of the Maillard³ type may be responsible and point to the blackening of the heated tobacco in support of this suggestion; but in addition it may be mentioned that the production of dark and humic substances by the direct action of organic acids on reducing sugars is well known.⁴ Table IV gives some results obtained in the Government Laboratory for certain of the acids and sugars

known to be present in tobacco. Some preliminary work, still mainly of a qualitative nature, has been carried out on the volatile end-products of these reactions associated with the heating of tobacco. It is certain that the loss in weight, or apparent moisture, is for the main part accounted for by the liberation of water itself. There is little, if any, carbon dioxide, but

TABLE I

APPARENT PERCENTAGE OF MOISTURE IN HOMOGENISED BRIGHT VIRGINIA TOBACCO

A series of 10-g samples dried at 100° C for 17 hours

%					
11-63	11-59	11-66	11-59	11-59	11-60
11-62	11-56	11-63	11-61	11-58	11-63
11-59	11-52	11-61	11-58	11-58	11-61
11-56	11-58	11-54	11-55	11-55	11-59
11-61	11-55	11-63	11-48	11-53	11-55
11-56	11-56	11-53	11-52	11-49	11-57
11-56	11-58	11-53	11-55	11-55	11-59
11-63	11-59	11-55	11-56	11-57	11-61

some organic matter of an aldehydic nature is evolved which is not formaldehyde. It is trapped by concentrated sulphuric acid, with which it reacts to form an insoluble carbonaceous residue. Further work is in progress on this aspect of the problem.

TABLE II

APPARENT PERCENTAGE OF MOISTURE IN HOMOGENISED BRIGHT VIRGINIA TOBACCO

10-g samples dried under varied conditions

Treatment	Loss in weight %
1. 17 hours drying at 60° C with 4 litres/min. air flow	8-62
2. 17 hours drying at 100° C with 4 litres/min. air flow	11-91
3. 17 hours drying at 100° C with 0-05 litres/min. air flow	13-37
4. 30 hours heating at 100° C followed by 17 hours drying at 100° C with 4 litres/min. air flow	16-62

Sufficient evidence is available therefore to show that the operation of heating tobacco for any appreciable period at a temperature of about 100° C results not only in the removal of all or part of the moisture originally present, but also in a chemical reaction in which moisture is produced. As may be expected, the component of the total apparent moisture accounted for by the results of chemical decomposition varies not only, as has been shown,²

TABLE III

EFFECT OF OVEN CONDITIONS ON THE COMPOSITION* OF HOMOGENISED BRIGHT CIGARETTE TOBACCO

	Dried at 60° C, %	Dried at 100° C for 17 hours	
		With immediate full ventilation, %	After pretreatment of 17 hours at 100° C without ventilation, %
Total soluble matter	48-8	45-6	44-0
Total insoluble matter	42-7	43-1	40-8
Apparent moisture	8-4	11-3	15-1
Sum of above	99-9	100-0	99-9
Reducing sugars	13-2	9-5	4-3
Total sugars	16-3	11-9	4-6
Free acid (ml of 0-1N NaOH per 10g tobacco)	72	64	53
Light petroleum ext.	2-75	2-77	2-66
Total nitrogen	1-47	1-39	1-32
Nicotine	1-51	1-23	1-20
Free ammonia	0-12	0-09	0-02
Nitrogen, other than ammonia and nicotine nitrogen	1-11	1-10	1-10
Resins	1-88	1-80	1-76

* For the analytical methods used, see appendix, p. 31.

with the degree of ventilation, but also with the temperature attained (Fig. 4) and with the time during which the tobacco is held at that temperature (Fig. 5). Other considerations, which have effects fortunately of a minor order, are the rate of initial heating of the sample and the barometric pressure within the oven. Thus it is apparent that the use of ovens to determine the moisture in tobacco does not result in the determination of anything that can

TABLE IV

EFFECT OF HEATING MIXTURES OF 1 G OF VARIOUS ORGANIC ACIDS WITH 5 G OF EITHER LAEVULOSE OR GLUCOSE FOR 36 HOURS IN A DRYING OVEN AT ABOUT 96° C

Sugar	Acid	Loss, %	Colour	Effervescence	Residue
Glucose	Malic	3.7	Straw	nil	Soluble
"	Citric	4.5	Straw	nil	Soluble
"	Oxalic	16.4	Black	Much	Soluble
"	Protein hydrolysate	16.6	Black	Much	Soluble
Laevulose	Malic	8.5	Dark brown	nil	Soluble
"	Citric	9.4	Dark brown	nil	Soluble
"	Oxalic	27.4	Black	Little	Insoluble
"	Protein hydrolysate	12.1	Black	Much	Partly insoluble

Sufficient water was added to ensure solution of the reagents, but the loss-in-weight percentages quoted below are based on the weight of the residue compared with the sum of the weights of the sugar and acid ingredients only.

be called the "true moisture" of the sample. The most to be expected from oven determinations is a series of consistent and repeatable figures in which the effect of oven decomposition is minimised and standardised. But, as for revenue purposes the loss-in-weight on drying at 212° C remains the legal moisture content of tobacco, the Government Laboratory and presumably the trade in general will continue to use oven drying; hence it may be of interest to describe briefly the type of apparatus that is in use for moisture determination to-day and the requirements that have led to the present design. It is clear that the major considerations must be—

- (1) Ventilation sufficient to ensure that at no time is evaporation from the surface of the tobacco itself slowed down, or the unavoidable chemical reactions allowed to occur at a high rate of velocity in the liquid phase.
- (2) Constancy of final temperature within the oven.
- (3) Identity of heat history for all the samples during the process of drying.
- (4) Speed in dealing with a large number of samples.
- (5) Economy of the time of skilled operatives, which in effect means drying overnight so that the working period may be devoted to weighing. This requirement itself necessitates that the oven shall be fully automatic.

If the heating of an individual sample pan placed in a hot oven is considered, it is clear that heat may reach it by one of three paths—contact with the ambient air, conduction through metal, or radiation from the surrounding surfaces. Some early experiments carried out in the Government Laboratory indicated that the heat flow through the air, though not negligible, contributes only slowly to the rise in temperature of the sample. Conduction through metal is important, but is likely to become uncertain as the pristine surface of the metal suffers from routine use. Radiation from surrounding surfaces is probably the largest and most consistent contributor to the considerable amount of heat required to raise the temperature of the sample and supply energy for the evaporation of moisture. To ensure identity of heat history for each sample, the Government Laboratory has found it necessary to construct ovens in which each pan is equidistant from the radiating surfaces and in which the whole of the internal surface is at the same temperature. In such an oven there is no balancing out of hot and cold spots as is necessary with, for instance, electric ovens of the normal type, and assurance can be felt that not even for short periods is any sample exposed to radiation from surfaces at a higher temperature than that finally attained by the whole oven. Acknowledgment must be made of the great help of the Imperial Tobacco Company, Limited, in this connection. In 1936, Dr. Jollyman of that company showed us an apparatus embodying an oven consisting of a cylindrical shell heated by an outer steam jacket; and

although his successors and ourselves have introduced modifications, his apparatus is very little different in essence from that shown in Fig. 6, which is a diagram of one of the ovens now in use in the Government Laboratory.

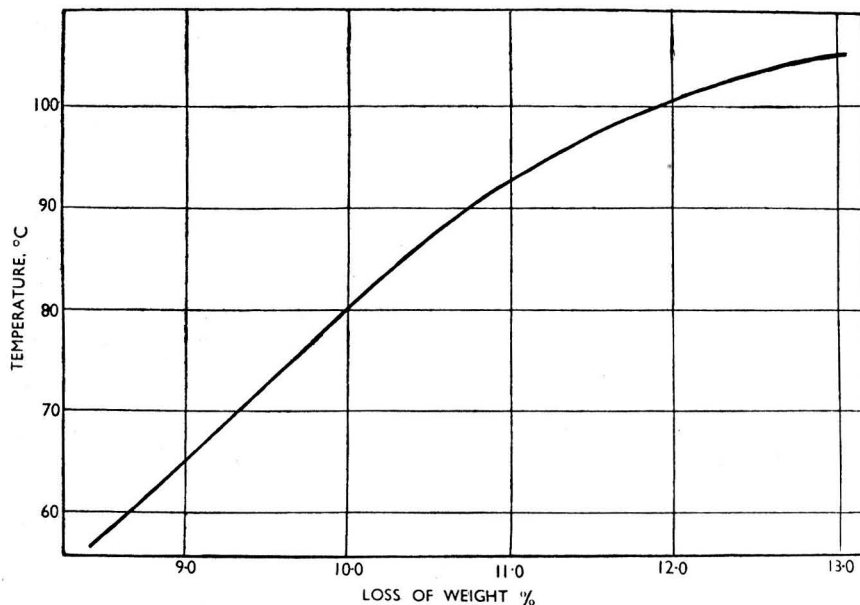


Fig. 4. Variation of decomposition with temperature; drying time 17 hours

In this device the oven proper is the central chamber, circular in plan, into which an internal movable rack (on which a number of sample pans are arranged symmetrically in tiers) is lowered. Up the central axis of the oven rises a perforated tube, distributing radially a flow of preheated air forced in by a centrifugal pump (not shown). Round the bottom, sides, and top of the chamber circulates a flow of steam generated from a container of distilled water below, into which the condensate returns. With ovens of this type, replicate determina-

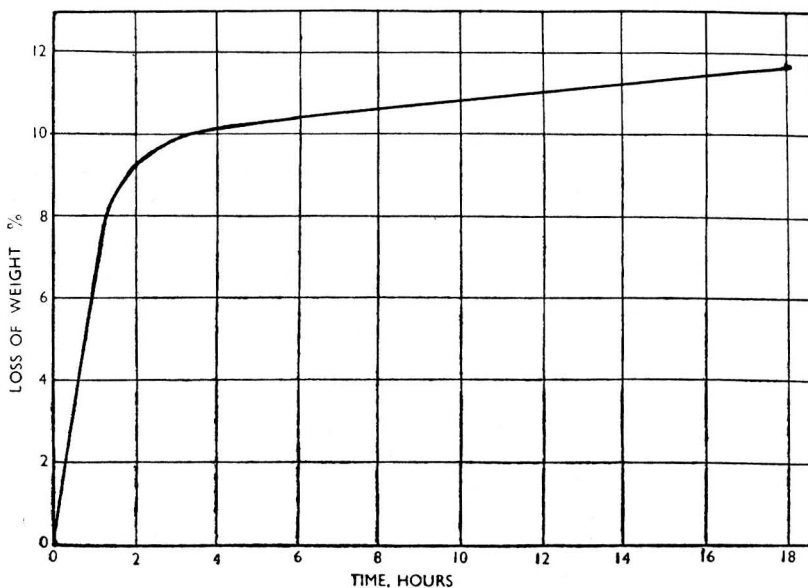


Fig. 5. Variation of decomposition with time at 100°C

tions having a degree of repeatability of the order of those shown in Table I may be confidently expected as a routine operation.

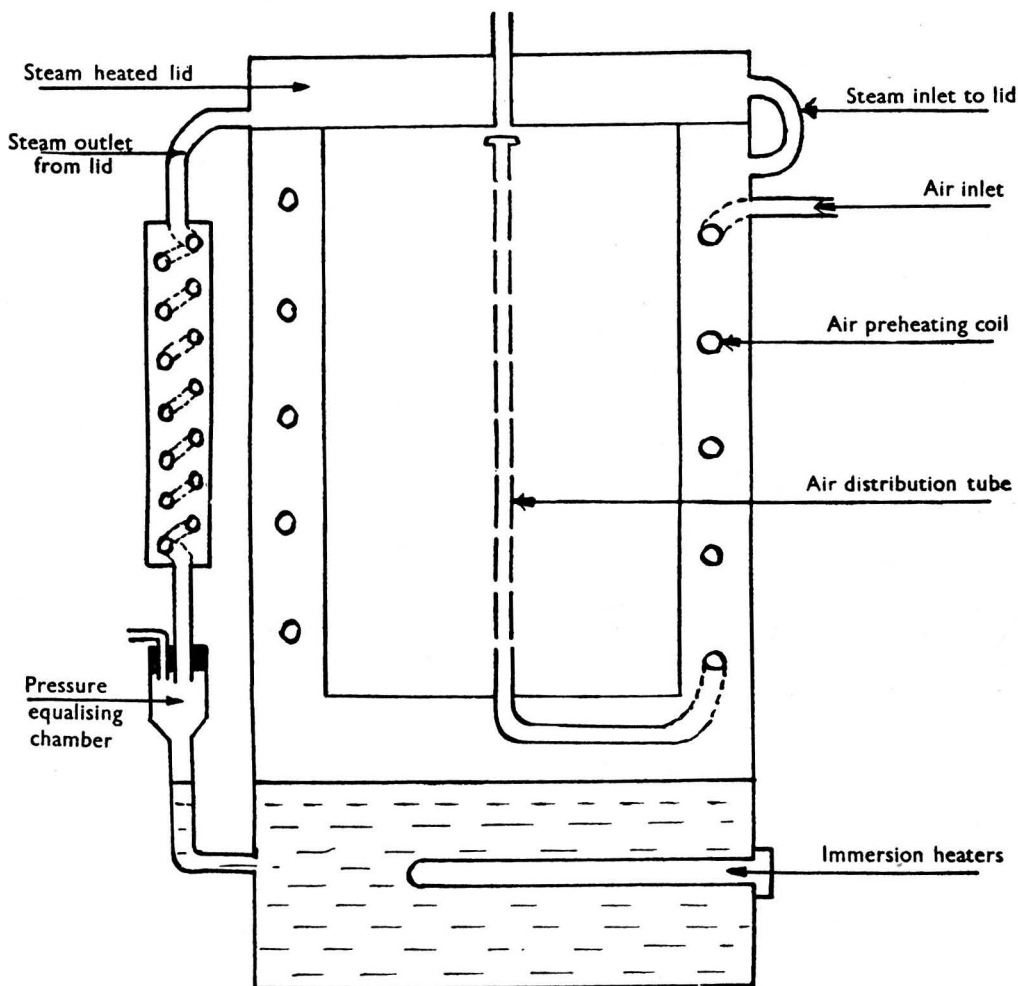


Fig. 6. Diagram of oven in use

An apparatus including some of the features of such an oven is the subject of a patent application made at the instance of the Imperial Tobacco Company, Limited, and quoted by Iles and Sharman.²

APPENDIX

NOTES ON THE METHODS USED IN OBTAINING THE DATA IN TABLE III

Nicotine—Five grams of tobacco is steam distilled with 2 g of magnesium oxide and 50 g of sodium chloride, and 250 ml collected. A further 5 ml is collected and tested for absence of nicotine. A 100-ml aliquot is acidified and the nicotine is precipitated with silicotungstic acid. The precipitate is filtered through a Gooch crucible, ignited, and weighed.

Light petroleum extract—Tobacco, 13.33 g, is in contact with 100 ml light petroleum for 18 hours. 75 ml of supernatant liquor is removed and evaporated on steam. Final residue is heated at 100° C for 1½ hours.

Total nitrogen—One gram of tobacco, 10 g of potassium sulphate, 0.5 g of copper sulphate and 20 ml of concentrated sulphuric acid are boiled in a Kjeldahl flask for 4 hours or until clear. The solution is then diluted, neutralised with sodium hydroxide, distilled into 25 ml of 0.1 N sulphuric acid and titrated back.

Reducing sugars—Tobacco, 12.1 g, is digested with 150 ml of water overnight. The mass is made up to 200 ml with silicotungstic acid, 12 per cent. solution; 100 ml of filtrate is then treated with 10 ml of neutral, 30 per cent. lead acetate solution. After filtration through a Buchner funnel, 100 ml is collected, 5 ml of saturated potassium oxalate is added, the solution made up to 110 ml and again filtered (Solution A). This solution is used to titrate Fehling's solution, using methylene blue as indicator.

Total sugars—As above, but 50 ml of Solution A is boiled for 30 seconds with 3 or 4 drops of concentrated hydrochloric acid and made up to 100 ml after cooling.

Total soluble—Five grams of tobacco is digested with 150 ml of water overnight. The mass is filtered through a Buchner funnel and washing continued until 1000 ml of extract is obtained. 100 ml of extract is dried for 1½ hours on a steam-bath.

Total insoluble—Fibrous matter from the above is carefully removed and dried at 100° C to constant weight.

Ammonia—Five grams of tobacco, 20 ml of 1 : 4 hydrochloric acid and 20 ml of silicotungstic acid, 12 per cent. is made up to 100 ml with water, 50 ml of filtrate collected, distilled with sodium hydroxide into 15 ml of 0.1 N sulphuric acid and titrated back.

Resins—Five grams of tobacco is digested with 100 ml of ethanol overnight, 50 ml of filtrate evaporated to dryness and digested with water. After re-filtration, the insoluble resins are dried at 100° C and weighed.

We wish to thank our colleagues in the Government Laboratory for help in the preparation of this paper, and the Government Chemist for permission to publish.

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DISCUSSION

MR. L. G. BECKETT pointed out that there was a considerable amount of oxygen at a pressure of 1 cm of mercury, and this could account for the blackening of the tobacco leaf in spite of the authors' contention to the contrary. He drew attention to the necessity for care when referring to degrees of vacuum. He considered it essential that any remark concerning pressure should be qualified by the words "gauge" or "absolute" to avoid difficulties that may be experienced by other workers in interpreting results.

DR. J. H. HAMENCE asked if the new oven really reached a temperature of 100° C.

MR. FRYD replied that it did. If the oven was empty it would reach 100° C in a very short time indeed. When the oven was fully loaded with about 100 samples, it would take from 2½ to 4 hours—depending naturally upon the water content of the sample material—to reach 100° C.

DR. HAMENCE said that the meeting had served a valuable purpose because it had brought the air flow methods to the notice of the Society. The latest conclusions for the estimation of water suggested that the air flow method was superior to other available methods.

Some Further Observations on the Analysis of Nylon Type Polymers

BY J. HASLAM AND M. CLASPER

Methods have been devised for the analysis of mixtures of hexamethylene diamine dihydrochloride and 5-amino caproic acid hydrochloride that may be obtained on the application to certain types of nylon polymer of the methods of hydrolysis previously reported by the authors. The method for the determination of the 5-amino caproic acid hydrochloride is based on titration with standard alkali, phenolphthalein being used as indicator; the method of determination of hexamethylene diamine dihydrochloride depends on the passage of a solution of the mixed hydrochlorides through a column of Amberlite IRA 400 resin and titration of the hexamethylene diamine passing through the column with standard alkali, methyl orange being used as indicator.

Samples of polymer produced (*a*) by the interaction of hexamethylene diisocyanate and 1 : 4-butanediol and (*b*) from ω -amino undecanoic acid have been submitted to hydrolysis by hydrochloric acid solution and the hydrolytic products examined along the lines laid down for nylon type polymers in the previous paper.

As a result of our work on the examination of nylon and related polymers,¹ it seemed to us that methods for the examination of mixtures of hexamethylene diamine dihydrochloride and 5-amino caproic acid hydrochloride would be extremely useful.

THE RESOLUTION OF MIXTURES OF HEXAMETHYLENE DIAMINE DIHYDROCHLORIDE AND 5-AMINO CAPROIC ACID HYDROCHLORIDE

We have been able to show that 5-amino caproic acid hydrochloride may be readily determined in mixtures of 5-amino caproic acid hydrochloride and hexamethylene diamine dihydrochloride by titration of the aqueous solution of the hydrochlorides with 0.1 *N* sodium hydroxide solution, phenolphthalein being used as indicator. Known weights of the two hydrochlorides were dissolved in 20 ml of water and the solution was titrated with 0.1 *N* sodium hydroxide, phenolphthalein being used as indicator. One millilitre of 0.1 *N* sodium hydroxide is equal to 0.01675 g of 5-amino caproic acid hydrochloride. The results are shown in Table I.

TABLE I

RECOVERY OF 5-AMINO CAPROIC ACID HYDROCHLORIDE FROM SYNTHETIC MIXTURES WITH HEXAMETHYLENE DIAMINE DIHYDROCHLORIDE

Composition of mixture		5-Amino caproic acid hydrochloride recovered, g
Hexamethylene diamine dihydrochloride, g	5-Amino caproic acid hydrochloride, g	
nil	0.5014	0.4989
0.1512	0.3494	0.3469
0.2512	0.2496	0.2479
0.3496	0.1489	0.1503
0.5021	nil	0.0017

Further, a method has been devised for the determination of hexamethylene diamine dihydrochloride in mixtures of hexamethylene diamine dihydrochloride and 5-amino caproic acid hydrochloride. The method is based on the passage of an aqueous solution of the hydrochlorides through a column of Amberlite IRA 400 ion-exchange resin. We are indebted to Dr. K. W. Pepper of the Chemical Research Laboratory, Teddington, for the suggestion that this resin might prove to be useful for our purpose. The hexamethylene diamine passing through the column is finally titrated with 0.1 *N* hydrochloric acid solution, methyl orange being used as indicator.

ION-EXCHANGE METHOD—

The method is as follows: 10 g of Amberlite IRA 400 dried at 100° C are mixed into a slurry with water and transferred to an ion-exchange column, Fig. 1. The excess of water is then run off until the resin in the column is just covered with water. At all times care must be taken to ensure that the liquid in the column is not drained beneath the head of the ion-exchange resin: the passage of air into the resin impairs the absorption capacity.

The Amberlite IRA 400 resin is activated by passing about 800 ml of *N* sodium hydroxide through the column at a rate of about 2 to 3 ml per minute. The apparatus and the resin are then washed with water until 50 ml of effluent give a titration of less than 0.1 ml of 0.1 *N* hydrochloric acid, methyl orange being used as indicator. Normally, about 250 ml of wash water are sufficient. The ion-exchange column is now ready for use; it must be used immediately after the water washing has been completed.

About 0.5 g of the mixed hydrochlorides is weighed, dissolved in 50 ml of water and the solution transferred to the separating funnel, A. This solution is allowed to pass through the column at a rate of 2 to 3 ml per minute. The separating funnel and sides of the column are carefully washed down with water, the washings being allowed to pass through the column. When this washing has been completed the separating funnel is filled with water, which is allowed to pass through the column at a steady rate of 2 to 3 ml per minute. The first 150 ml of effluent are collected and titrated with 0.1 *N* hydrochloric acid, methyl orange being used as indicator, and each succeeding 50 ml of effluent are collected and similarly titrated until the titre is less than 0.1 ml of 0.1 *N* hydrochloric acid.

The combined titres are then calculated to a percentage of hexamethylene diamine dihydrochloride in the mixture by means of the following factor—

1 ml of 0.1 *N* hydrochloric acid \equiv 0.009457 g of hexamethylene diamine dihydrochloride

Application of the above method to five mixtures of hexamethylene diamine dihydrochloride and 5-amino caproic acid hydrochloride gave the results shown in Table II. The titres of the successive volumes of liquid passing through the columns are also shown.

TABLE II

RECOVERY OF HEXAMETHYLENE DIAMINE DIHYDROCHLORIDE FROM SYNTHETIC MIXTURES WITH 5-AMINO CAPROIC ACID HYDROCHLORIDE

MIXTURES TAKEN—	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Hexamethylene diamine dihydrochloride, g	0.5013	0.3510	0.2520	0.1502	nil
5-Amino caproic acid hydrochloride, g. . .	nil	0.1480	0.2471	0.3490	0.4997
TITRE, ML OF 0.1 <i>N</i> HYDROCHLORIC ACID—					
Effluent, ml:					
150	51.86	35.70	25.52	15.12	0.23
50	0.29	0.28	0.18	0.08	0.06
50	0.23	0.18	0.10		
50	0.06	0.08	0.06		
Total titre, ml	52.44	36.24	25.86	15.20	0.29
Hexamethylene diamine dihydrochloride					
{ added, g	0.5013	0.3510	0.2520	0.1502	nil
{ found, g	0.4958	0.3427	0.2445	0.1437	0.0027

Although the results for the recovery of hexamethylene diamine dihydrochloride are slightly low, we have found that the above method when used in conjunction with the direct titration method for the determination of 5-amino caproic acid hydrochloride, p. 33, is extremely valuable in the examination of the hydrolysis products of interpolymers of nylon 66, 610 and 6.

NOTES ON THE ION-EXCHANGE METHOD—

(i) The volume of sodium hydroxide solution used to generate the active base from the Amberlite IRA 400 is extremely large, but in our experience the use of smaller volumes of sodium hydroxide solution or faster rate of passage of the sodium hydroxide solution through the column is accompanied by a reduction in efficiency.

(ii) Other proprietary resins have been tried in place of Amberlite IRA 400, but without success. When De-Acidite F was used, the removal of excess alkali by washing with water after the initial activation was much more difficult than when Amberlite IRA 400 was used. When an aqueous solution of hexamethylene diamine dihydrochloride was passed through an

activated Amberlite IRA 400 column, the recovery of hexamethylene diamine in the effluent was almost theoretical. When the corresponding experiment was carried out with De-Acidite F, although the recovery of hexamethylene diamine in the effluent was reasonably in agreement with theory, it was extremely difficult to reach finality in the process. When experiments were carried out by passage of aqueous solutions of 5-amino caproic acid hydrochloride through activated columns of Amberlite IRA 400, the proportion of base in the effluent titratable to methyl orange indicator was negligible. With the De-Acidite F, however, successive volumes of effluent gave distinct positive titrations to methyl orange indicator. These titrations were of the order of 1.5 ml of 0.1 *N* hydrochloric acid per 50 ml of effluent.

EXAMINATION OF POLYMER PRODUCED BY THE INTERACTION OF HEXAMETHYLENE DIISOCYANATE AND 1 : 4-BUTANEDIOL

The polymer produced by the interaction of hexamethylene diisocyanate and 1 : 4-butanediol appears to be known to the trade as Igamide "U" or Perlon.² The sample melted at 179° C and had a nitrogen content (macro-Kjeldahl) of 10.58 per cent. The infra-red spectrum was as shown in Fig. 2*a*.

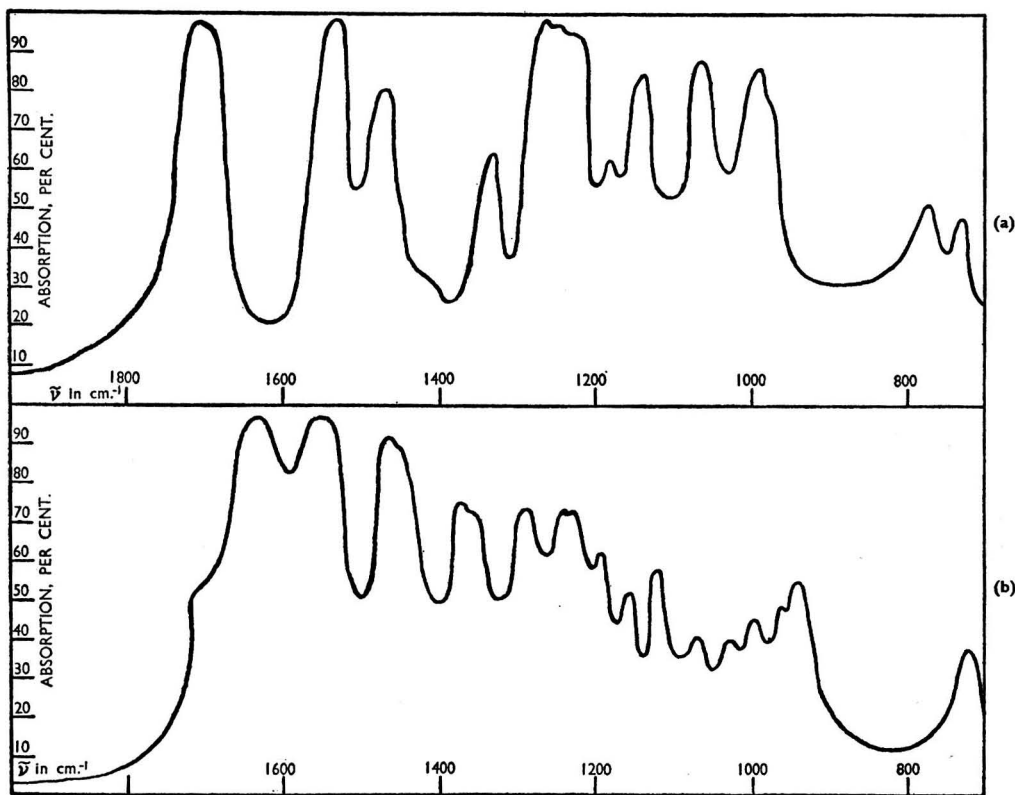


Fig. 2. Infra-red spectra of polymers (a) produced by the interaction of hexamethylene diisocyanate and 1 : 4-butanediol, and (b) produced from ω -amino undecanoic acid

Considerable attention has been paid to the identification of the products of hydrolysis of this type of polymer, and the following experiments were carried out.

Experiment 1—The sample, 5 g, was hydrolysed with 200 ml of 50 per cent. v/v hydrochloric acid for 60 hours. The hydrolysis product had the characteristic odour of a chlorinated hydrocarbon. A Dean and Stark apparatus was then fitted to the flask and the solution was boiled for 2 hours. At the end of this time a small amount of immiscible liquid was collected at the bottom of the graduated side arm. This part of the apparatus was disconnected when cool, and the upper liquid in the graduated arm was removed by a suction pipette. The recovered liquid remaining in the Dean and Stark apparatus was washed

successively with about 2 ml of water until the wash water was neutral to litmus; five washings were required. The washed liquid was transferred to a 2-ml centrifuge tube, a small amount of sodium sulphate (anhydrous) was added and the whole allowed to stand overnight. The dried liquid had a boiling-point of 154.5°C , a refractive index of 1.4556 and a chlorine content of 55.25 per cent. These figures were consistent with the material being 1:4-dichlorobutane, characteristic figures for which are: boiling-point, 155.0°C , refractive index at 20°C , 1.4566, and chlorine content, 55.84 per cent.

Experiment 2—In a second experiment 15 g of the sample were hydrolysed with 600 ml of 50 per cent. v/v hydrochloric acid in the apparatus shown in Fig. 3. As the hydrolysis proceeded, a layer of immiscible liquid began to accumulate in the side arm. The liquid in this side arm was run off from time to time and separated in a separating funnel. The

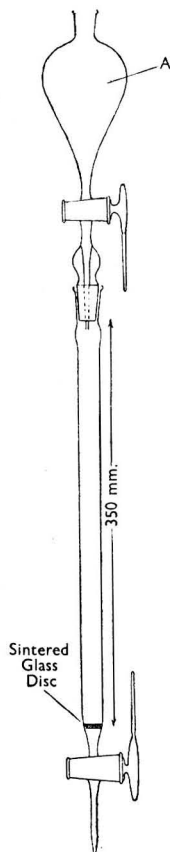


Fig. 1. Ion-exchange column

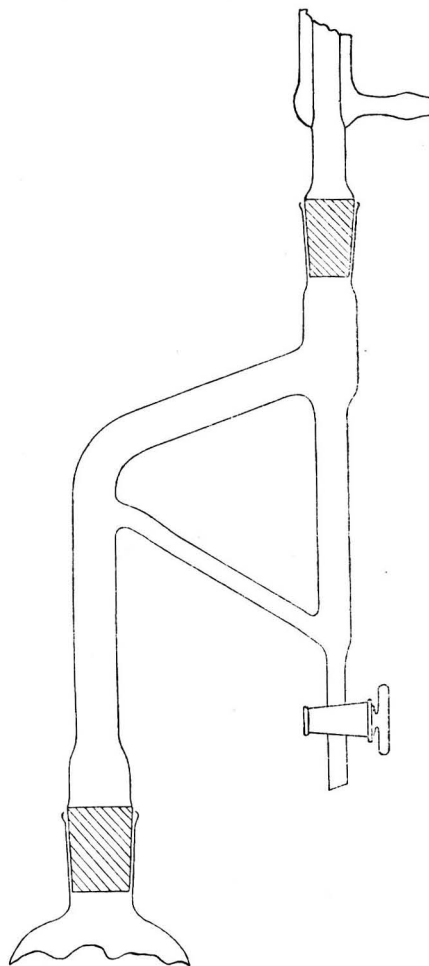


Fig. 3. First apparatus for hydrolysis

upper layer was reserved and the lower layer returned to the hydrolysis flask. After about 24 hours, approximately 2.5 ml of upper layer had been obtained, and this liquid was dried overnight with anhydrous potassium carbonate. The dry liquid was then distilled in a small side-arm distillation flask. Three fractions were collected of the following approximate boiling ranges and amounts—

				Boiling range, $^{\circ}\text{C}$	Volume, ml
Fraction 1	63 to 65	0.6
Fraction 2	65 to 70	1.3
Fraction 3	Above 70 (boiled mainly at 150°C)	0.6

A micro-analytical examination of these fractions gave the following carbon, hydrogen and chlorine figures—

	Carbon, %	Hydrogen, %	Chlorine, %
Fraction 1	64.0	9.3	1.4
Fraction 2	65.4	9.8	0.3
Fraction 3	49.8	7.2	24.4

The figures for carbon, hydrogen and chlorine contents of the fractions pointed strongly to the presence of a large proportion of tetrahydrofuran in fraction 2 and a rather smaller proportion in fraction 1. Tetrahydrofuran was known to oxidise with nitric acid to give succinic acid, and fractions 1 and 2 were therefore oxidised with nitric acid, authentic tetrahydrofuran being oxidised similarly as a control, in the following manner.

Half a millilitre of water and 0.2 ml of the fraction were taken in a test tube and cooled in ice-cold water. The cold liquor was added to 2 ml of ice-cold concentrated nitric acid and the mixture left standing overnight in a beaker of ice and allowed to come slowly to room temperature. The nitric acid solution was evaporated to dryness on the water-bath in a tared evaporating basin and the residue moistened once or twice with water previous to re-evaporation. After drying at 100° C for 1 hour, a white crystalline residue was obtained which had the following properties—

	Fraction 1	Fraction 2	Tetrahydrofuran
Melting-point, °C	182 to 187	185 to 188	185 to 187
Equivalent weight	59.2	59.5	59.6

The figures for succinic acid are—

Melting-point, 185° C
Equivalent weight, 59.05

As a result of the above experiment we concluded that the hydrolysis of this type of polymer with 50 per cent. v/v hydrochloric acid under the above conditions produced an appreciable proportion of tetrahydrofuran. At the same time we concluded from Experiment 1 that when the action of hydrochloric acid was prolonged, 1:4-dichlorobutane could also be isolated from the hydrolysis products.

Experiment 3—A further 1 g of the sample was hydrolysed for 60 hours with 50 per cent. v/v hydrochloric acid, and the aqueous solution was filtered and the filtrate was taken to dryness on a water-bath. The residue was then purified by dissolving in alcohol, boiling with animal charcoal, filtering and re-precipitating by adding acetone to the cold alcohol solution. This procedure was repeated three times and the precipitate finally obtained was dried under vacuum.

The material so obtained melted at 252° C, and micro-analytical examination gave the following ultimate analyses: carbon, 38.15 per cent.; hydrogen, 9.5 per cent.; nitrogen, 14.6 per cent.; chlorine, 37.60 per cent.

Corresponding figures for hexamethylene diamine dihydrochloride are as follows: melting-point, 253° C; carbon, 38.10 per cent.; hydrogen, 9.6 per cent.; nitrogen, 14.81 per cent.; chlorine, 37.49 per cent.

We now sought to use the information we had obtained as a result of the three experiments to develop a test which could be applied in a simple way to samples suspected to be of this type of polymer. Such a test is described below as applied to 1 g of a sample.

One gram of the polymer was hydrolysed by boiling with 20 ml of 50 per cent. v/v hydrochloric acid in the apparatus shown in Fig. 4. There was little visible change in the appearance of the dispersion during the first 24 hours of boiling. It was necessary to shake the flask and contents from time to time so that the whole of the sample was removed from the sides of the flask and subjected to hydrolysis. After 24 hours the particles in suspension appeared to become much finer and this process continued. After about 48 hours the mixture appeared to clear to a certain extent and the hydrolysis was then continued for a further period of 12 hours, that is, a total of 60 hours. At the end of this period the solution was a pale brownish colour and contained a small amount of material in suspension.

After hydrolysis for about one hour the liquid in the condenser and siphon began to assume an oily appearance, and after three hours a distinct layer of oily liquid was visible at point A, Fig. 4, above the aqueous layer in the siphon. At this stage, *i.e.*, on the appearance of an oily upper layer in the siphon, the liquid in this tube, including the aqueous layer,

was withdrawn by means of a capillary pipette. After hydrolysis for a further 3 hours a second oily upper layer was formed in the siphon and this also was withdrawn and added to the original distillate. The combined distillates were cooled in ice-cold water and added to 2 ml of ice-cold concentrated nitric acid contained in a test tube. The test tube was then

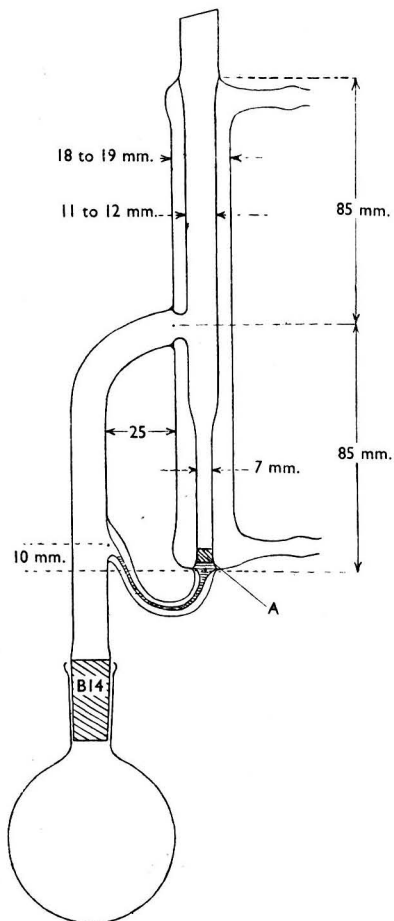


Fig. 4. Second apparatus for hydrolysis

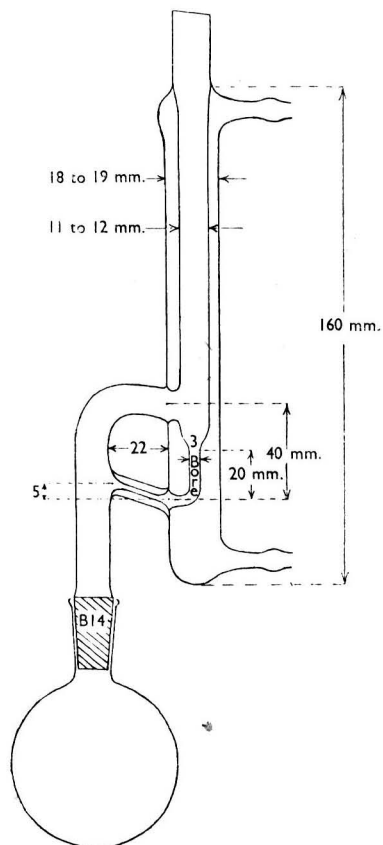


Fig. 5. Modified apparatus for hydrolysis

All dimensions in millimetres

placed in a beaker containing iced water and the whole left overnight. As the ice melted there was a gradual increase of temperature until room temperature was reached and also a gradual increase in colour of the solution from colourless to yellowish-green. On the following morning the nitric acid solution was evaporated to dryness on the water-bath and the test was completed as described under *Experiment 2*, p. 37.

The white crystalline residue so obtained weighed 0.0763 g, had a melting-point of 185° to 187° C and an equivalent weight of 59.4 as determined by semi-micro titration in alcoholic solution with 0.02 N sodium hydroxide and phenolphthalein indicator.

The pale brownish coloured hydrochloric acid solution from the hydrolysis was filtered through a tared sintered glass crucible No. 1, G3, and the residue well washed with water prior to drying at 100° C. The dry residue weighed 0.0170 g. The hydrochloric acid filtrate was evaporated to dryness in a tared evaporating basin and dried to constant weight at 100° C. This residue weighed 0.7258 g and had a melting-point of 248° to 254° C and a chlorine content of 36.6 per cent.

We have shown that the principle of the above test can be applied to as little as 0.5 g of sample by use of the modified apparatus shown in Fig. 5.

EXAMINATION OF POLYMER PRODUCED FROM ω -AMINO UNDECANOIC ACID

Within recent months we have been called upon to examine several samples of a nylon-type material that has been proved to consist of the so-called polymer "R".³ This polymer has also been described as type 11 nylon, *i.e.*, the polymer made from ω -amino undecanoic acid by the removal of the elements of water. The infra-red spectrum of the polymer is shown in Fig. 2*b*.

We have found that this polymer is attacked by 50 per cent. v/v hydrochloric acid, and when 0.5 g of an authentic sample of the polymer was boiled under reflux for 40 hours with 20 ml of 50 per cent. v/v hydrochloric acid and the solution subsequently cooled, a crystalline deposit was formed. The hydrolysis product possessed a characteristic odour. The hydrolysis product was transferred with the aid of about 20 ml of water to the apparatus for continuous ether extraction¹ and the solution extracted with ether for approximately 6 hours. The ether extract was evaporated to dryness and the residue dried at 100° C and weighed. The solution of the hydrochlorides was evaporated to dryness, dried to constant weight at 100° C and weighed. The melting-point and chlorine content of the residual hydrochlorides were determined, and the equivalent weight was calculated from the results of the titration of the hydrochlorides with standard alkali, phenolphthalein being used as indicator. In addition, carbon, hydrogen and nitrogen in the original polymer were also determined, as well as the melting-point.

From this examination the results shown in Table III were obtained.

TABLE III

EXAMINATION OF 0.5-G SAMPLE OF POLYMER PRODUCED FROM ω -AMINO UNDECANOIC ACID*Polymer—*

Nitrogen, 7.01%; carbon, 70.95%; hydrogen, 11.76%
Melting-point, 185° to 186° C

Hydrolysis products of polymer—

	1	2
Ether extract of hydrolysed product	4.1%	5.7%
Residue after evaporation of ether extracted hydrolysis products	125.2%	122.5%

Base hydrochloride—

Melting-point of base hydrochloride	145° to 147° C	146° C
Chlorine in base hydrochloride	14.52%	14.65%
Equivalent weight of base hydrochloride (calculated from phenolphthalein titre)	245.8	242.0

OBSERVATIONS ON THE DATA IN TABLE III—

(i) The nitrogen, carbon and hydrogen figures are not in strict agreement with those we should expect to obtain for the pure polymer obtained from ω -amino undecanoic acid by removal of one molecule of water. The theoretical figures for this pure polymer would be: nitrogen, 7.64 per cent.; carbon, 72.06 per cent.; hydrogen, 11.54 per cent.

(ii) The melting-point of the sample examined was 185° to 186° C. We have encountered samples of this polymer of rather lower melting-point, *i.e.*, about 180° C.

(iii) The proportion of ether extract and hence of residual base hydrochloride do not agree. Infra-red examination has indicated that this ether extract consists essentially of the base hydrochloride, *i.e.*, the hydrochloride of ω -amino undecanoic acid. This hydrochloride is slightly soluble in ether and the varying results are due to the fact that the throughput of ether is not the same in the duplicate extractions.

(iv) There is a certain amount of evidence to support the view that the hydrolysis product of this polymer does not consist completely of the hydrochloride of ω -amino undecanoic acid. In our experience there is present in the hydrolysis a rather flocculent material that is to a certain extent insoluble in water and which is almost certainly present as an impurity in the base hydrochloride. This would account for the fact that the figures obtained are not in strict agreement with theory. The theoretical figures for the chlorine content of ω -amino undecanoic acid hydrochloride and its equivalent weight are: chlorine content, 14.91 per cent.; equivalent weight, 237.8.

We are indebted to Mr. H. Willis for the infra-red spectra of the two polymers and to Mr. N. Payne for his assistance in the design of the apparatus used in the examination of polymers produced by the interaction of hexamethylene diisocyanate and 1 : 4-butanediol.

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The Determination of Acetyl Values for Use in Component Fatty Acid Analyses of Castor Oils

By J. P. RILEY

A comparison has been made between the British Standards Institution (second method) and the Association of Official Agricultural Chemists' methods for the determination of acetyl values, and it has been concluded that both procedures give very similar results. Where results of high accuracy are required several determinations should be made and the mean calculated. A procedure has been developed for the complete analyses of castor oils and tested by application to mixtures of fatty acids of known composition.

NUMEROUS methods have been proposed for the determination of the acetyl value of fats, most of which are based either on direct acetylation of the oil in the cold with a mixture of pyridine and acetic anhydride and subsequent determination of the amount of acetic anhydride consumed,^{1,2} or on acetylation with boiling acetic anhydride and determination of the acetic acid obtained by hydrolysis of the resultant acetyl compound.^{3,4}

The former method suffers from the defect that the end-point of the titration is rather vague and many modifications have been suggested for increasing the accuracy,^{5,6,7} but for the ultimate purpose of component acid determination direct acetylation with acetic anhydride alone has been found preferable.

In the present study a comparison has been made between the British Standards Institution (second method)³ and the Association of Official Agricultural Chemists' methods⁴ for the determination of acetyl values, both of which depend on the determination of the saponification values of the oil and the acetylated oil. It has been found that both methods give very similar results, but it is suggested that where results of high accuracy are required the saponification values both of the oil and its acetyl compound should be the mean of at least five determinations. The accuracy of the B.S.I. method has been tested by using pure specimens of methyl ricinoleate and methyl 12-hydroxystearate; and it is concluded that with care results having an accuracy of ± 1 per cent. can be obtained.

The acetyl value method, when applied to castor oils, does not give a true estimate of the amount of ricinoleo-glycerides present, since small amounts (about 0.6 per cent.) of 9 : 10-dihydroxystearo-glycerides that are present⁸ are also estimated. The dihydroxystearic acid may be determined with sufficient accuracy by crystallisation of the mixed fatty acids of the oil (after removal of unsaponifiable matter by the S.P.A. method⁹) from ethyl acetate at 0° C. The precipitated dihydroxystearic acid, which has only a low solubility under these conditions, is weighed after filtration and washing, and to this weight is added a correction for its slight solubility in the ethyl acetate used as solvent and wash liquor. Knowledge of the acetyl value and percentage of dihydroxystearic acid enables the percentage of ricinoleic acid in the oil to be calculated. Besides ricinoleic acid, the other principal constituent of castor oils is linoleic acid, which occurs to the extent of about 4 to 6 per cent. The linoleic

acid occurring in castor oil has been identified as the normal 9 : 12-linoleic acid of seed fats (J. P. Riley, unpublished observation). It may be determined by spectrophotometric examination of the mixed acids (after removal of unsaponifiable matter), after alkali isomerisation at 180° C for 60 minutes under the conditions of Hilditch *et al.*¹⁰ It is not necessary to make a correction for the absorption due to ricinoleic acid since it has been shown that ricinoleic acid treated under these conditions shows negligible absorption. Oleic and saturated acids, which occur in small amounts in the oil, are determined by iodine value and by difference respectively.

As a test of the proposed method for the analysis of castor oils, mixtures have been made up from pure methyl ricinoleate, oleate and linoleate and analysed by the recommended procedure with results which agree with the calculated values.

EXPERIMENTAL

PREPARATION OF PURE ACIDS AND ESTERS—

Methyl ricinoleate—Brown and Green¹¹ first prepared methyl ricinoleate by low temperature crystallisation, but attempts to repeat their work were unsuccessful. After a study of a number of solvents it was concluded that acetone was the most suitable, but that the solubility of methyl ricinoleate in it varied greatly with temperature. Crystallisations were therefore carried out by slowly cooling the solution to a temperature at which the desired amount of solid had separated and then maintaining it at this temperature for 3 hours.

A commercial cold drawn castor oil (600 g, I.V. 82.9) was hydrolysed and the unsaponifiable matter extracted. The recovered acids were methylated at room temperature. The neutral esters (566 g) were crystallised from acetone first in 11 per cent. solution at -50° C and then in 9 per cent. solution at -40° C. The soluble product (341 g) from the latter crystallisation was then recrystallised three times in 5 per cent. solution in acetone at -65° C, -50° C and finally at -70° C, by which means there resulted 190.7 g of methyl ricinoleate S.E. 311.2 (S.E. (theory) 312.0), I.V. 80.0 (I.V. (theory) 81.2), n_D^{25} 1.4657, n_D^{40} 1.4603.

Ricinoleic acid—Methyl ricinoleate (1.88 g) was hydrolysed by boiling for 10 minutes with 10 ml of 10 per cent. alcoholic potash. The soaps were acidified with dilute sulphuric acid, and the liberated acids extracted with ether. Most of the ether was removed by distillation, and the last trace *in vacuo* at room temperature. Yield of ricinoleic acid 1.73 g, I.V. 83.8 (I.V. (theory) 85.2), $E_{1\text{cm}}^{1\%}$ at 234 m μ after alkali isomerisation at 180° for 60 minutes, 1.1.

Methyl 12-hydroxystearate—Commercial cold drawn castor oil was alkali refined by washing with 10 per cent. potassium hydroxide solution and then hydrogenated with Raney nickel catalyst at 100° C. The product (I.V. 2.4) was saponified and the resultant acids (90 g) were ground up and extracted in a Soxhlet extractor with light petroleum (b.p. 40° to 60° C) for 25 minutes. The residue (86 g) was recrystallised three times in 1 per cent. solution in petroleum (b.p. 60° to 80° C) yielding 69 g of 12-hydroxystearic acid, m.p. 82° C. The acid (20 g) was esterified at room temperature with methyl alcohol containing 0.5 per cent. of hydrogen chloride, yielding 19.7 g of methyl 12-hydroxystearate which after crystallisation from acetone at -20° C had m.p. 57.5° to 58° C (Grummitt and Siedschlag¹² record 56° to 57° C).

9 : 10-Dihydroxystearic acid—The mixed acids (296 g) from 304 g of castor oil were dissolved in 1500 ml of ethyl acetate and cooled to 0° C. After standing overnight at 0° C, the precipitated dihydroxystearic acid (1.36 g) was filtered off and twice recrystallised from 50 ml of ethyl acetate at 0° C, yielding 1.01 g of 9 : 10-dihydroxystearic acid, m.p. 141° to 142° C.

Determination of the solubility of dihydroxystearic acid—Dihydroxystearic acid (0.5 g) was stirred at 0° C for 3 hours with 550 ml of redistilled ethyl acetate, and the solution was filtered through a cooled sintered glass filter. 500 ml of the filtered solution was evaporated to dryness in a platinum basin, leaving 0.0925 g of dihydroxystearic acid; whence the solubility of dihydroxystearic acid is 0.0185 g per 100 ml of ethyl acetate at 0° C.

Methyl oleate—Methyl oleate prepared as described by Hilditch and Pathak¹³ had the following characteristics—I.V. 84.8, $E_{1\text{cm}}^{1\%}$ at 234 m μ after alkali isomerisation at 180° C for 60 minutes 4.3, whence its component acid composition was—saturated 1.6 per cent., oleic 97.9 per cent. and linoleic 0.5 per cent. by weight.

Methyl linoleate—A concentrate of linoleic acid obtained by low temperature crystallisation of the mixed fatty acids of a sunflower seed oil was methylated and fractionated. The

fraction having I.V. 165.3, $E_{1\text{cm}}^{1\%}$ at 234 μ after alkali isomerisation at 180° C for 60 minutes 796, was used in the investigation. The component acids of the sample, calculated from the above data were: oleic 12.1 per cent., linoleic 87.9 per cent. by weight.

DETERMINATION OF ACETYL VALUE BY B.S.I. AND A.O.A.C. METHODS—

Saponification equivalent—Weigh out 3 g of the oil (or 1.5 g of the acetylated oil) into a 300-ml flat-bottomed flask, and add 25 ml of neutral alcohol, followed by 50 ml of approximately 0.5 N alcoholic potash. Heat the mixture under reflux for 2 hours and then titrate with 0.5 N sulphuric acid using phenolphthalein as indicator. Run a blank determination under the same conditions but omitting the sample.

Acetyl value—Acetylate 15 g of the oil as described in B.S.S. 684 (1950). Carry out saponification value determinations on both the oil and its acetyl compound in quintuplicate and calculate the acetyl value according to the formula:

$$\text{Ac.V.} = \frac{S' - S}{1 - 0.00075S}$$

where S is the mean sap. value of the oil

S' is the mean sap. value of the acetylated oil.

All the saponification tests in the text and tables of this paper are recorded as saponification equivalents (S.E.), and not as in the B.S.I. and A.O.A.C. specifications as saponification values. The formula for converting saponification equivalents to saponification values is—

$$\frac{56,100}{\text{S.E.}}$$

COMPARISON OF THE B.S.I. AND A.O.A.C. METHODS FOR THE DETERMINATION OF ACETYL VALUES

A neutralised commercial castor oil and the methyl esters prepared from another castor oil were examined by both the B.S.I. and A.O.A.C. methods with the results shown in Table I.

TABLE I

COMPARISON OF B.S.I. AND A.O.A.C. ACETYL VALUE METHODS

	Oil S.E.	Acetylated oil		Methyl esters S.E.	Acetylated methyl esters	
		B.S.I. S.E.	A.O.A.C. S.E.		B.S.I. S.E.	A.O.A.C. S.E.
	309.3	180.8	179.3	314.3	189.1	189.3
	310.8	180.4	179.7	312.9	188.0	189.1
	309.7	181.3	179.6	312.0	188.7	188.7
	310.2	181.6	180.5	313.4	187.5	189.4
	310.0	181.1	180.2	312.7	187.8	188.3
	310.6			312.5	188.7	189.3
Mean	310.2	181.0	179.9	313.0	188.3	189.0
Mean deviation	0.14%	0.17%	0.22%	0.20%	0.27%	0.19%
Standard deviation	0.566	0.469	0.707	0.787	0.624	0.436
Acetyl value	—	149.3	152.4	—	137.1	135.8

From the above results it will be seen that both methods give very similar results and that the determined acetyl values do not differ from the mean by more than 1 per cent. For consistency in the later parts of the work, the B.S.I. method has been employed.

EXAMINATION OF METHYL RICINOLEATE AND METHYL 12-HYDROXYSTEARATE BY THE B.S.I. METHOD

The accuracy of the adopted method has been further tested by the examination of pure samples of methyl ricinoleate and methyl 12-hydroxystearate with the results shown in Table II.

The figures shown indicate that there is good agreement between the determined and calculated saponification equivalents and acetyl values. The determined acetyl values are

about 0.6 per cent. low, but it is impossible to say whether this is due to an error in the method, or to the presence of small amounts of impurities in the esters used as standards.

COMPLETE ANALYSIS OF CASTOR OILS

Dissolve about 60 to 80 g of the castor oil in 300 ml of ether and neutralise it by washing with 10 per cent. aqueous potassium hydroxide and then with water till free from alkali. Divide the neutral oil into two portions.

(i) Use 30 g for the determination of acetyl value.

(ii) Saponify 30 to 40 g of the oil by boiling for 1 hour with excess of 10 per cent. alcoholic potash, extract the unsaponifiable matter with ether and determine it according to the S.P.A. method⁹ (with volumes increased proportionately). Liberate the fatty acids from the soaps with dilute sulphuric acid and extract them with ether, remove the ether by distillation. Divide the resultant acids into two portions. Use the first portion (2 g) for

TABLE II
EXAMINATION OF PURE ESTERS BY B.S.I. PROCEDURE

	Methyl ricinoleate		Methyl 12-hydroxystearate	
	Ester	Acetylated ester	Ester	Acetylated ester
Number of determinations	5	5	2	2
S.E. mean	311.2	177.3	313.8	178.4
S.E. theory	312.0	177.0	314.0	178.0
Mean deviation	0.12%	0.13%	0.06%	0.06%
Standard deviation	0.510	0.374	—	—
Acetyl value (found)		157.4		156.7
(theory)		158.5		157.6

the determination of linoleic acid by alkali isomerisation at 180° C for 60 minutes followed by spectrophotometric examination at 234 m μ by the method of Hilditch *et al.*¹⁰ Dissolve the remaining portion of the acids (about 25 to 35 g) in 10 ml of ethyl acetate for each gram of acids and cool to 0° C overnight. Filter the precipitated dihydroxystearic acid through a cooled, weighed sintered glass filter (porosity 3), wash it with a known volume (about 30 ml) of cold ethyl acetate in small portions. Dry the washed precipitate in a vacuum desiccator under high vacuum and weigh. The product consists of substantially pure dihydroxystearic acid and should have a melting-point of not less than 139° C (pure 9 : 10-dihydroxystearic acid has m.p. 141° to 142° C). In calculating the percentage of dihydroxystearic acid in the mixed fatty acids, a correction must be made for its solubility (0.0185 g per 100 ml at 0° C) in the known volume of ethyl acetate used as solvent and wash liquor.

Calculations—Percentage of triacetylricinolein in the acetylated oil—

$$\frac{\text{Ac.V.} \times 100}{159.1} = P.$$

The percentage of ricinoleic acid in the mixed fatty acids of the oil is different from the above because of the change in molecular weight on acetylation. It can be calculated with sufficient accuracy by means of the following approximation

$$\text{Let } \frac{298P}{352.7} + 0.96(100 - P) = y$$

Then, if the proportion of ricinoleic acid in the mixed fatty acids is R per cent.

$$R = \frac{298P \times 100}{352.7y}$$

This figure for ricinoleic acid is too high, since it includes the contribution of the two hydroxyl groups in the dihydroxystearic acid also present. Let the percentage of the latter = D. Then the actual percentage of ricinoleic acid = R - 2D.

Oleic acid is determined by its iodine value after making allowance for the ricinoleic and linoleic acids. Saturated acids are determined by difference.

The proposed method for the analysis of castor oils has been tested by the examination of two mixtures of methyl ricinoleate, oleate and linoleate in known amounts, with the results shown in Table III.

TABLE III
EXAMINATION OF MIXTURES OF KNOWN COMPOSITION

	Mixture 1		Mixture 2	
	found	calc.	found	calc.
Esters	308.7	310.2	306.6	308.7
S.E.	0.16%	—	0.08%	—
S.E. mean deviation	183.1	183.5	189.4	190.9
S.E. acetyl compound	0.23%	—	0.07%	—
S.E. mean deviation	144.4	144.3	131.3	129.6
Acetyl value	86.0	85.5	90.0	90.1
Iodine value				
Mixed acids:				
Iodine value	89.5	89.5	93.9	94.3
$E_{1\text{cm}}^{1\%}$ at 234 m μ (180°/60 min.) ..	38.4	39.9	82.9	83.3

Whence the component esters of the mixtures are—

	found		found	
	% (wt.)	% (wt.)*	% (wt.)	% (wt.)*
Methyl ricinoleate	90.1	90.0	80.0	80.9
Methyl oleate	5.7	5.6	11.2	9.9
Methyl linoleate	4.2	4.4	8.8	9.2

* Calculated on the assumption that the composition of methyl oleate and linoleate concentrates are: saturated ester 1.6%, methyl oleate 97.9% and methyl linoleate 0.5%; and methyl oleate 12.1% and methyl linoleate 87.9% (wt.) respectively. See page 41.

An example of the analysis of a commercial cold drawn castor oil of B.P. quality by the proposed procedure is given below—

Characteristics of alkali refined oil—S.E. 309.7; I.V. 82.9; Ac.V. 150.2; n_D^{25} 1.4778; n_D^{40} 1.4741; $[\alpha]_D^{20} + 4.42^\circ$. Acetylated oil, S.E. 180.5.

The refined oil (50.57 g) yielded 0.244 g of unsaponifiable matter and 46.32 g of mixed fatty acids, which gave 0.1681 g of dihydroxystearic acid, m.p. 139° C (corrected weight 0.261 g).

Mixed acids after removal of unsaponifiable matter—I.V. 87.0; $E_{1\text{cm}}^{1\%}$ at 234 m μ (after alkali isomerisation at 180° for 60 minutes) 48.5.

The component fatty acids of the oil calculated from these results are—saturated 0.9; oleic *nil*; linoleic 5.4; ricinoleic 92.6; dihydroxystearic 0.6; unsaponifiable 0.5 per cent. by weight.

Further application of the method to castor oils from various sources will be reported elsewhere.

The author thanks Professor T. P. Hilditch, F.R.S., for his criticism and guidance during this work.

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The Determination of Small Amounts of Hydroquinone

BY R. BELCHER AND W. I. STEPHEN

A method is described for the determination of small amounts of hydroquinone in the presence of methacrylic acid. The solution containing hydroquinone is allowed to react with an excess of ferric ammonium sulphate and the ferrous iron produced is treated with *o*-phenanthroline and determined absorptiometrically. The interference of the ferric iron unconsumed in the reaction is avoided by conversion to the ferrifluoride ion.

HYDROQUINONE is used as an inhibitor in the polymerisation of methacrylic acid, and it is often necessary to determine the amounts present at various stages of the reaction. None of the methods available for the determination of hydroquinone was sufficiently sensitive to determine accurately the small amounts present under our conditions (1 to 200 μg), and it became necessary to find an entirely new method. Several reactions are known whereby various substances are determined colorimetrically after treatment with hydroquinone; hence it seemed possible that by suitable modification, the same reactions might be exploited for the determination of hydroquinone itself.

Hydroquinone has been used to determine the following substances colorimetrically: silver,¹ copper² and nitrite.³ It has also been used to reduce ferric iron to the ferrous state before determining iron colorimetrically by its reaction with *o*-phenanthroline.⁴ All these reactions were examined in turn, but only the last proved to be suitable for the determination of hydroquinone.

The basis of the reaction is as follows. Excess of a ferric salt is added to the solution containing hydroquinone. The ferric salt is reduced with the production of an amount of ferrous iron equivalent to the amount of hydroquinone originally present. *o*-Phenanthroline is added, and the amount of ferrous iron is determined colorimetrically after suppressing the colour due to the excess ferric iron by addition of a suitable complexing agent. A visual comparison method based on this principle was first developed, and a brief note on its use has appeared elsewhere.⁵ More recently another method has been described for the determination of similar amounts of hydroquinone based on the formation of molybdenum blue by reduction of a solution containing phosphotungstate.⁶ The present method uses a Spekker absorptiometer for the measurement of the colour intensity and is, accordingly, much more accurate than the visual comparison method.

THE DETERMINATION OF FERROUS IRON—

As the first step in the development of the method, solutions containing ferrous iron were used to find the optimum conditions for maximum colour development. Graphs were prepared, by using 0.5-cm, 1-cm and 2-cm cuvettes, relating the amount of ferrous iron present to the drum reading. An Ilford spectrum blue filter No. 602 was used, with the instrument set at 1.0 against water. It was found that a period of 30 minutes was required at a pH between 3 and 4 for the maximum colour development. The correct pH range was obtained by adding suitable amounts of sodium acetate solution.

A straight line relationship between the amount of ferrous iron and the drum reading was found under these conditions (Figs. 1, 2 and 3).

THE EFFECT OF FERRIC IRON—

Since an excess of ferric iron would necessarily be present in an actual determination, it would be expected to interfere unless its effect could be eliminated in some way. Suitable amounts were added to solutions containing known amounts of ferrous iron, and the latter was then determined. Although the interference was not marked, it was sufficient to affect the accuracy of the determination. However, it was found that the interference could be eliminated by complexing the ferric iron by the addition of ammonium fluoride.

THE DETERMINATION OF HYDROQUINONE—

Known amounts of hydroquinone were allowed to react with ferric iron for various times, the solution then being treated with *o*-phenanthroline and the intensity of colour

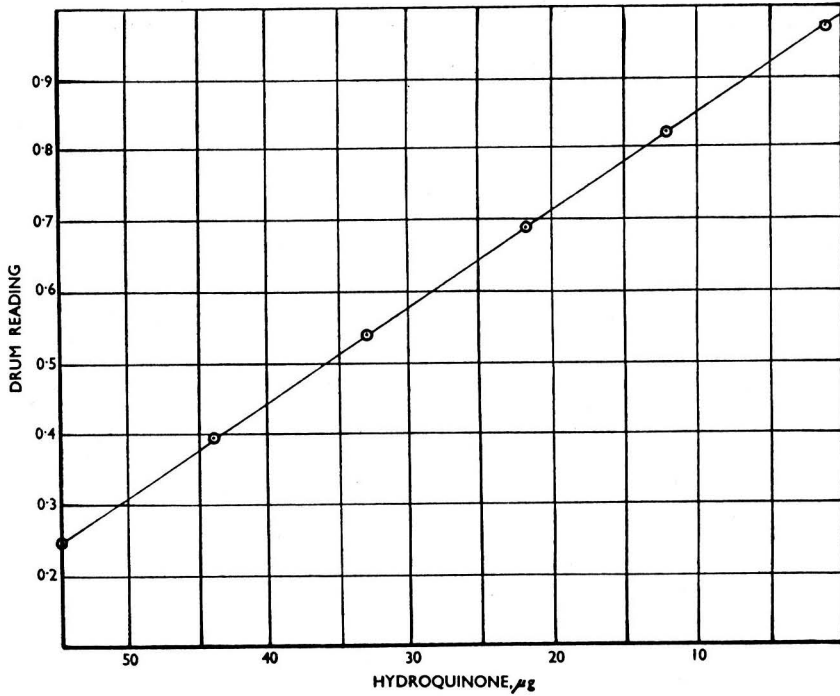


Fig. 1. Graph obtained with 2-cm cuvette

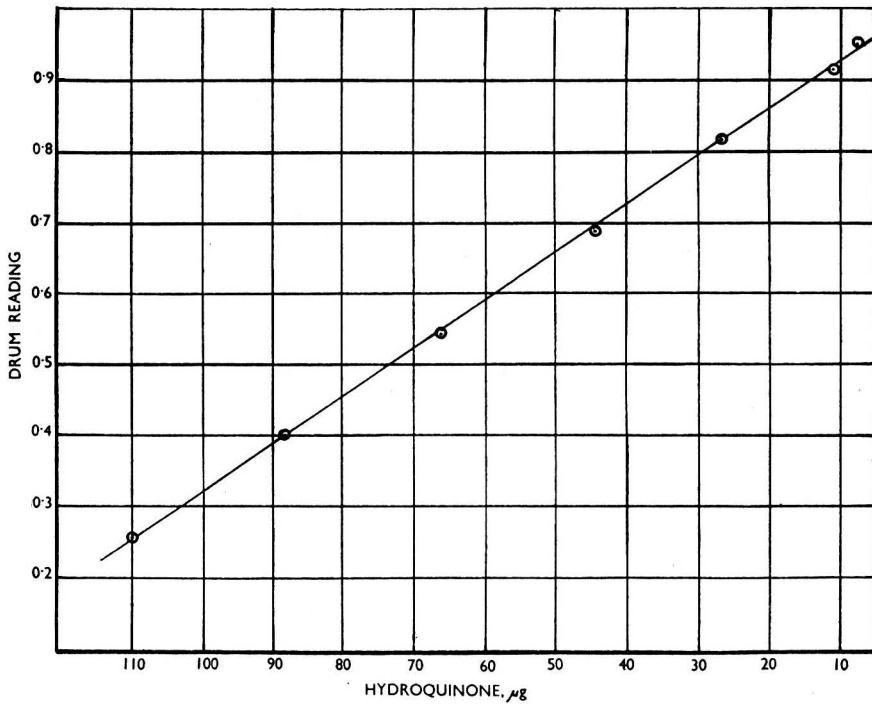


Fig. 2. Graph obtained with 1-cm cuvette

measured after complexing the excess ferric iron with ammonium fluoride. A reaction time of 30 minutes was found necessary for complete oxidation of the hydroquinone by the ferric iron. Under these conditions the reaction was found to proceed quantitatively, and hence it was possible to prepare the standard graphs by using a solution of ferrous ammonium

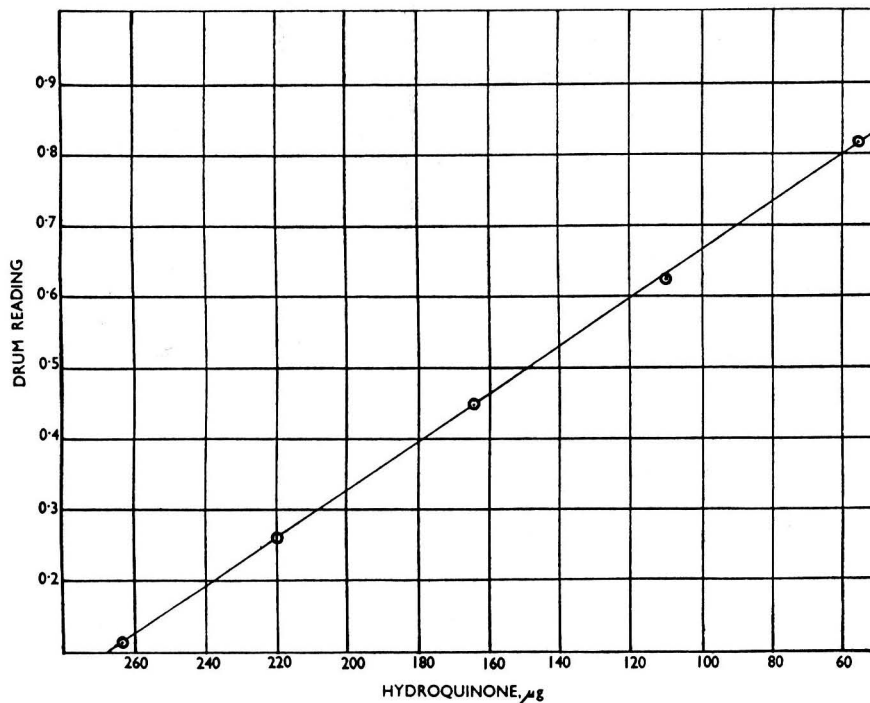


Fig. 3. Graph obtained with 0.5-cm cuvette

sulphate instead of a solution of hydroquinone. The equivalent amount of hydroquinone is calculated on the basis that 2 molecules of ferrous ammonium sulphate are equivalent to 1 molecule of hydroquinone.

Some results are shown in Table I and indicate that the method is sufficiently accurate for a determination of this type.

TABLE I

THE DETERMINATION OF HYDROQUINONE IN THE ABSENCE OF METHACRYLIC ACID

Hydroquinone present, μg	Hydroquinone found, μg
275	272, 273
220	222, 221
165	164
110	112, 110
55	56
44	45
33	33
22	23
11	11
6	5
3	3
2	2
1	1

THE DETERMINATION OF HYDROQUINONE IN THE PRESENCE OF METHACRYLIC ACID—

The amount of methacrylic acid likely to be present in the solutions to be analysed was of the order of 2 to 3 ml of a 1 per cent. solution. Three-millilitre quantities of a 1 per cent. solution were added to various known amounts of hydroquinone and the latter was then determined. In every case a control determination was carried out in which the same

amount of hydroquinone was determined without the addition of methacrylic acid. From the results included in Table II it can be seen that the methacrylic acid has no effect on the determination.

TABLE II

THE DETERMINATION OF HYDROQUINONE IN THE PRESENCE OF 3 ML OF 1 PER CENT. METHACRYLIC ACID SOLUTION

Hydroquinone present,	Hydroquinone found	
	Methacrylic acid absent,	Methacrylic acid present,
μg 220	μg 220	μg 221
165	164	167
110	110	110
55	55	55
33	33	32
17	16	17
6	6	7
3	3	4
1	1	2

Some further tests were also carried out with much stronger solutions of methacrylic acid, 3 ml of an 8.6 per cent. solution being added. The results are included in Table III and show that the accuracy of the determination is not impaired by the presence of fairly large amounts of methacrylic acid.

TABLE III

THE DETERMINATION OF HYDROQUINONE IN THE PRESENCE OF 3 ML OF 8.6 PER CENT. METHACRYLIC ACID SOLUTION

Hydroquinone present,	Hydroquinone found	
	Methacrylic acid absent,	Methacrylic acid present,
μg 220	μg 220	μg 220
55	55	57
6	6	7
4	4	5

PROCEDURE FOR THE DETERMINATION OF HYDROQUINONE

REAGENTS—

Ferric ammonium sulphate—A 0.001 *M* solution containing 4 ml of 50 per cent. v/v sulphuric acid per litre.

Ammonium fluoride—A 0.1 *M* solution.

Sodium acetate—A 1 *M* solution.

o-Phenanthroline—A 0.1 per cent. aqueous solution.

PROCEDURE—

Transfer 5 ml of the solution to be analysed to a 25-ml graduated flask and add 5 ml of 0.001 *M* ferric ammonium sulphate. Add sufficient of the 1 *M* sodium acetate solution to bring the pH to 3.5 to 4. The appropriate amount should be determined beforehand by adding bromophenol blue indicator to separate quantities of ferric ammonium sulphate and hydroquinone solution, and noting the minimum amount required to give a blue colour to the solution.

Shake the flask to mix the solutions thoroughly and allow to stand for 30 minutes. Add 5 ml of 0.1 per cent. *o*-phenanthroline and after 5 minutes add 1 ml of 0.1 *M* ammonium fluoride solution and dilute the solution with water to the mark. It is essential to add the reagents in this order. Stand the solutions for 30 minutes and read the absorption on the Spekker absorptiometer with Ilford spectrum No. 602 filters and a setting of 1.0 to water.

PREPARATION OF THE GRAPH—

Prepare solutions of ferrous ammonium sulphate of the concentration required by appropriate dilution of a 0.2 *M* solution containing 4 ml of 50 per cent. v/v sulphuric acid

per litre. Maintain the same acid concentration in the diluted solutions. Transfer suitable amounts to a 25-ml graduated flask. Adjust the pH as described above, add 5 ml of 0.1 per cent. *o*-phenanthroline and dilute the solution to the mark. Allow the solutions to stand for 30 minutes and then take the absorptiometer reading as before. Convert the amounts of ferrous iron present to the equivalent amounts of hydroquinone and prepare graphs relating concentration to drum reading. Prepare graphs for the 0.5-cm, the 1.0-cm and the 2.0-cm cuvettes.

Thanks are due to Mr. T. S. West for independently carrying out a large number of check determinations.

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DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
BIRMINGHAM

May, 1950

The Determination of Gold, Palladium and Platinum by Dithizone

By R. S. YOUNG

A volumetric method has been devised for the determination of small amounts of gold, palladium and platinum by the dithizone extraction method. The procedure is rapid in operation and applicable to the beads obtained in the assay of precious metals:

In the base metal industry the analysis of silver, gold and the platinum metals is usually carried out by separating these elements by means of a fire assay, or a combination of wet methods and fire assay, to give a bead containing all the silver, gold, and the platinum group metals in the sample. From this point the procedures generally recommended^{1,2,3} for the determination of the individual metals, gold, platinum, palladium, etc., are lengthy and often unsuitable for the very small quantities of these elements that may be present.

For some years diphenylthiocarbazono, generally abbreviated to dithizone, has been used in certain instances for the determination of small quantities of about a dozen metals and the procedures and literature have been reviewed in recent books.^{4,5} The method outlined below is an extractive titrimetric procedure employing dithizone, which should prove useful to many base metal laboratories that have occasion to carry out regularly a small number of precious metal determinations.

Gold, palladium and platinum form dithizonates when shaken with dithizone in dilute mineral acid solution. The end-point of the reaction is indicated by colour changes and the quantity of dithizone used gives an accurate measure of the metal present. Palladium can be separated from the other metals by extraction of its dimethylglyoxime complex with chloroform. Gold can then be extracted with dithizone from dilute hydrochloric acid solution, extraction of any silver present being prevented by addition of sodium bromide. Platinic chloride does not react with dithizone, and therefore platinum does not interfere in the gold titration provided that the solution is free from reducing agents. In dilute acid platinous chloride reacts quantitatively with dithizone and platinum can therefore be extracted with this reagent, after removal of the gold, by reducing the platinic to platinous chloride with stannous chloride.

REAGENTS—

Dithizone solutions—(a) Concentrated stock solution. Stir thoroughly 45 mg of dithizone powder with 200 ml of carbon tetrachloride, and filter into a 250-ml separatory funnel. Cover with 30 to 40 ml of sulphurous acid solution.

(b) Dilute standard solution. Dilute the stock dithizone solution ten times with carbon tetrachloride and standardise against weighed quantities of gold, palladium and platinum by the procedures described below. The solutions can conveniently contain 0.01 to 0.02 mg of gold, palladium or platinum per ml, and the value of the dilute standard dithizone solution will be approximately 1 ml = 0.01 mg of gold or platinum and 0.05 mg of palladium. The standard solutions can be made by dissolving the metals in aqua regia, evaporating to dryness, taking up in hydrochloric acid and diluting to appropriate volumes so that the hydrochloric acid concentration is about 1 per cent.

Stannous chloride—Dissolve 80 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 180 ml of warm hydrochloric acid and dilute with 300 ml of water. Place a stick of tin in the bottle to keep the solution in the reduced state.

PROCEDURE

PALLADIUM—

The starting material for this determination is the silver - gold bead, containing small quantities of the platinum group metals, obtained from a direct fire assay of an ore, or from a combination wet and dry assay of a concentrate, matte, blister copper, lead bullion, refinery slime, or similar product. After weighing the bead on the assay balance, place it in a 50-ml beaker, add 5 ml of 1 + 1 sulphuric acid, and fume strongly on a hot plate. The silver and palladium dissolve, but gold, platinum and the rest of the platinum metals remain unattacked as a black residue.

Cool, carefully dilute with water, and separate the soluble silver and palladium from the remaining metals by decanting the solution into a 100-ml separatory funnel and wash the insoluble residue with water by decantation. If the gold and insoluble platinum metals are so finely divided that it is impossible to separate and wash by decantation, filter through a small Whatman No. 40 paper with pulp, wash, dry and ignite the paper and residue in a small porcelain crucible.

To the solution containing the silver and palladium, in a volume of about 50 ml in the separatory funnel, add 2 ml of a 1 per cent. aqueous solution of dimethylglyoxime sodium salt. Allow to stand for 10 minutes, shaking the separatory funnel occasionally to speed the reaction. Extract the palladium glyoxime by shaking twice with 4 to 5-ml portions of chloroform and drawing off the lower layer into a 50-ml beaker. Evaporate the chloroform on the edge of a hot plate, add 3 to 4 ml of hydrochloric acid and 2 to 3 ml of nitric acid and evaporate to dryness.

Dissolve the palladium in 5 ml of hydrochloric acid with gentle heating, cool and transfer the solution to a 50-ml separatory funnel. Rinse the beaker with 15 ml of water so that the final concentration of hydrochloric acid is 25 per cent. Add 0.2 ml of stannous chloride solution and run in the standard dithizone solution from a 10-ml burette in small portions, shaking vigorously between additions and withdrawing the lower layer from the separatory funnel. When all the palladium has been extracted by dithizone the carbon tetrachloride layer in the funnel changes from the dull olive-green of palladium dithizonate to the unmistakably brilliant emerald green of dithizone in carbon tetrachloride.

If the palladium titration shows a colour change from olive-green to yellow near the end-point, it is probable that the reducing action of stannous chloride has been exhausted and the yellow oxidation product of dithizone is appearing. The addition of a drop or two of stannous chloride will restore the true green colour of unchanged dithizone, or the grey-green of palladium dithizonate.

The number of millilitres of standard dithizone used to extract the palladium is a measure of the quantity of the latter present. The dithizone is standardised against known quantities of palladium by the procedure used for the sample. The usual precautions regarding cleanliness of glassware and reagent blanks, which apply to all dithizone procedures, must be observed.

By a simple modification of the above procedure, palladium may be determined not only in the presence of silver, but also of gold and platinum. This is of importance, for instance, where the method used to decompose the sample or to part the assay bead leaves

gold, platinum and most of the palladium unattacked. Dissolve the mixed metals in dilute aqua regia and to the resulting solution containing silver, gold, platinum, palladium, etc., and about 0.2 ml of hydrochloric acid and 0.1 ml of nitric acid in a volume of 10 ml, add 2 ml of dimethylglyoxime solution and proceed as described above. The presence of the small quantity of nitric acid prevents precipitation of gold and co-precipitation of platinum with the palladium glyoxime. Retain the upper layer in the separatory funnel, after the withdrawal of the two chloroform extractions, for determination of the gold and platinum as described below.

GOLD—

Dissolve the residue of gold and platinum, obtained in parting the assay bead, in aqua regia, and evaporate the solution to dryness and take up the chlorides in a minimum quantity of hydrochloric acid. Dilute this solution or the solution of gold and platinum from which palladium has been removed by extraction with dimethylglyoxime and chloroform as described above, to 10 to 15 ml in a 50-ml separatory funnel, add 0.2 ml of hydrochloric acid and 0.1 ml of a 10 per cent. solution of sodium bromide and titrate with standard dithizone as in the palladium analysis, adding 0.2-ml portions at a time, shaking vigorously until the lower

TABLE I

	Synthetic solutions		Cupellation heads	
	Taken, mg	Found, mg	Taken, mg	Found, mg
Gold	0.017 0.022 0.030	0.016 0.021 0.032	0.025	0.023
Palladium	0.011 0.016 0.021	0.012 0.015 0.023	0.013	0.015
Platinum	0.012 0.018 0.029	0.013 0.017 0.027	0.021	0.020

layer shows the yellow colour of gold dithizonate, and withdrawing. Combine the additions, shaking and drawing off until the dithizone layer remains green, which indicates that all the gold has been extracted.

The addition of sodium bromide prevents the interference of silver, which if present, would also give a yellow dithizonate. Excessively long shaking may cause a slight fading of the dithizone colour at the end-point in the gold titration, since reducing agents must be absent to keep any platinum present in the platinic state. The dithizone is standardised against a known gold solution under the same conditions.

PLATINUM—

After removing gold, as described above, and drawing off any excess of dithizone from the separatory funnel, add sufficient hydrochloric acid to bring the acidity to 25 per cent. of concentrated acid, and then add 0.2 to 0.3 ml of stannous chloride solution, shake and allow to stand several minutes. Now titrate the platinum with standard dithizone as described above, until the carbon tetrachloride layer no longer acquires the light yellow colour of platinous dithizonate. The titration value of the dithizone solution is determined against a known platinum solution under the same conditions.

RESULTS

In material like assay beads, silver is usually determined by difference from the initial weight of the bead. The other platinum metals, osmium, rhodium, iridium and ruthenium, do not react with dithizone under the conditions described above. They will, therefore, be counted as silver in any difference calculation unless the gold and platinum metal residues are weighed after parting the bead.

Some typical results on synthetic solutions containing known quantities of gold, platinum and palladium are shown in Table I. In all the beads the quantity of silver present was equivalent to ten times the weight of the combined precious metals, but no other metals were present in more than traces. This condition is similar to that found in an assay bead.

Cupellation beads of known composition were also analysed by this procedure with the results shown in the table.

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RHODESIA COPPER REFINERIES LIMITED
NKANA, NORTHERN RHODESIA

December, 1949

Apparatus

APPARATUS FOR DISTILLATION ON A SEMI-MICRO SCALE

THIS apparatus, Fig. 1, is designed to carry out semi-micro operations involving distillation, fractionation and distillation under reduced pressure. One of the difficulties encountered in preparing or purifying small (0.5 to 1.5 ml) amounts of liquid is the loss of material inherent in the experimental method. This loss is due to the liquid that wets the comparatively large surface of the distillation apparatus and collecting vessel, together with the vapour that fills the distilling flask. The apparatus described considerably reduces this loss. Quantities of 1 ml or less may be distilled, the only loss being the volume of liquid that when volatilised would fill the apparatus to the top of the collecting cup.

DESCRIPTION AND USE OF APPARATUS

SIMPLE DISTILLATION—

The apparatus for simple distillation consists of a "cold finger" water condenser, A, to the bottom of which is fastened a detachable cup, B. The cup is provided with two glass hooks, C, which engage with two glass projections, D, on the bottom of A. The cup and condenser unit is fixed by means of a cork into the distillation tube, E, which is fitted with a thermometer pocket, F. A groove is cut in the cork in order to avoid any pressure rise during distillation. The liquid to be distilled is placed in E and gently boiled by means of a semi-micro burner, the condensate from the cold finger dripping into the collecting cup. Condensate from the outside of B is prevented from dripping on the thermometer bulb either by suitable positioning of the thermometer pocket or by providing the cup with a projection as shown. The condensate in B is cooled by the end of A, the water inlet tube of which is drawn out and extended to the bottom. The length of the thermometer pocket, F, is such that vapours condense before reaching the rubber sleeve holding the thermometer. In practice, since the diameter of the thermometer is only slightly less than the internal diameter of the side arm, the small amount of condensate trapped therein forms an effective vapour block. Aerial oxidation of the distillate is prevented by the vapour which jackets it. Thus aromatic amines such as *m*-toluidine can be distilled with very little, if any, aerial oxidation. For high-boiling liquids, adequate cooling of the condenser is obtained by half filling it with cold water and aspirating air through it by suction at G, by means of a filter pump or other suitable device.

The apparatus in this form may be used for organic preparations involving simple distillation, *e.g.*, preparation of the volatile acid chloride of an aliphatic acid by distillation of a mixture of the acid and a small excess of benzoyl chloride.¹ No drying tube is required, the acid chloride in the collecting cup being unaffected by atmospheric moisture during the short time required for the operation. Certain inorganic preparations involving distillation, such as the preparation of chromyl chloride, may also be conveniently carried out on a small scale with this apparatus.

Removal of the collecting cup converts the apparatus into the conventional semi-micro reflux apparatus. It may also be used for semi-micro sublimation.

VACUUM DISTILLATION—

The distillation tube of the apparatus can be modified for vacuum distillation by the provision of an air leak tube, H, and a tube, J, which can be connected to the vacuum pump via a manometer. The cup and condenser unit must be fitted to the distillation tube by means of a rubber stopper, and the thermometer pocket can be omitted if the distillation temperature is not required.

Omission of the air leak tube and collecting cup allows the apparatus to be used for semi-micro vacuum sublimation.

FRACTIONAL DISTILLATION—

For fractional distillation, a modified distillation tube is used. This is fitted with a small fractionating column, K, containing glass helices or other suitable packing. The liquid to be distilled is placed in the distillation tube, very gently boiled, and fractions distilling at the desired temperature are collected in the cup.

The apparatus described is an improvement on existing semi-micro distillation apparatus of a more conventional type. Small quantities of liquid can be distilled with little loss, and as the

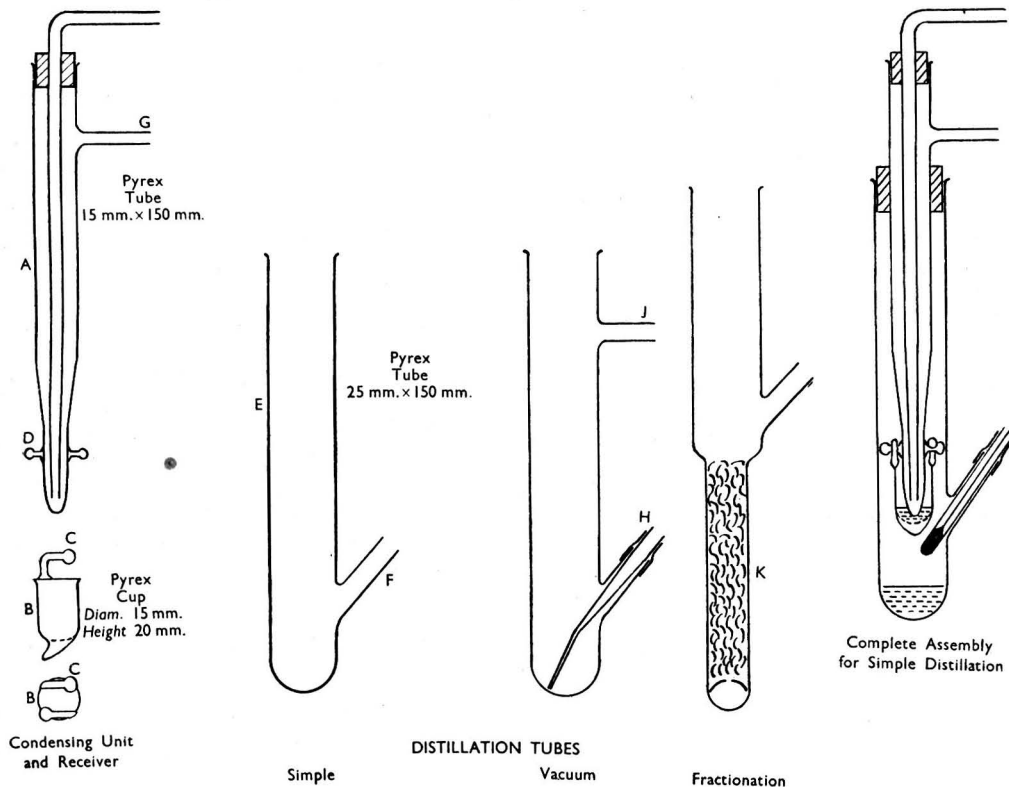


Fig. 1. Details of apparatus

distillate and vapour do not come into contact with the stopper, the apparatus is equivalent to one of all-glass construction. It may therefore be used to distil liquids which attack cork and rubber stoppers. Such liquids would normally require distillation apparatus of all-glass construction. The apparatus is inexpensive and may readily be made by any worker possessing moderate skill in glass blowing.

REFERENCE

1. Brown, H. C., *J. Amer. Chem. Soc.*, 1938, **60**, 1325.

DEPARTMENT OF PURE AND APPLIED SCIENCE
LOUGHBOROUGH COLLEGE, LEICS.

JOSEPH M. CONOLLY
GRAHAM OLDHAM
June, 1950

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1950, 75, 690).

<i>Public Analyst</i>	<i>Appointments</i>
HARRAL, James Charles (Deputy)	County Borough of Dēwsbury.
HARRAL, James Charles	Borough of Harrowgate.
HAMENCE, Jack Hubert (Joint)	Borough of Chingford.
JONES, Daniel Evans	Borough of Neath.
JONES, William Elwyn (Deputy)	County of Worcestershire.
TAYLOR, George (Joint)	Borough of Chingford.
WOOD, Eric Charles	County of East Suffolk.

NOTIFICATION of the following appointment has been received from the Department of Health for Scotland since the last record in *The Analyst* (1950, 75, 690).

<i>Public Analyst</i>	<i>Appointment</i>
DAVIES, David Richard Aylmer (Additional)	County of Kirkcudbright.

OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1950, 75, 690).

<i>Agricultural Analyst</i>	<i>Appointments</i>
CAHILL, Terence John (Deputy)	County Borough of Carlisle.
TURNER, Mervyn Edward Dennah (Deputy)	County of Hereford.

Ministry of Food

CIRCULAR MF 19/50

We are informed by the Ministry of Food in this circular, dated 31st October, 1950, that it is proposed to notify the Trade through the Food Manufacturers' Federation that the Code of Practice on the composition and labelling of flour mixtures which is produced as C.P.6 on page 49 of the report "The Advertising, Labelling and Composition of Food," published in September, 1949, will be withdrawn with effect from 30th April, 1951.

British Standards Institution

NEW SPECIFICATIONS*

B.S. 1428 : 1950. Microchemical Apparatus. Price 2s. each part.

Part A1—Carbon and Hydrogen combustion train (Pregl type).

Part D2—Washout pipettes.

Part D3—Micro-nitrometer (Pregl type).

Group A of the series comprises combustion trains for the determination of elements.

Group D of the series includes volumetric microchemical apparatus; part D1 was published in 1938 as B.S. 846, Part 3: Burettes with pressure filling device and automatic zero.

B.S. 1672 : 1950. Methods of testing rubber latex. Price 2s.

* Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and may be obtained on application to the Secretary, Miss D. V. Wilson, 7-8, Idol Lane, London, E.C.3.

Draft Specifications prepared by Technical Committee PVC/1—Pigments, Sub-Committee PVC/1/10—Miscellaneous Pigments.

CM(PVC) 6656—Draft Revision of B.S. 314, Ultramarine Blue and Violet for Paints.

CM(PVC) 6657—Draft Revision of B.S. 318, Green Oxide of Chromium for Paints.

Draft Specification prepared by Technical Committee NFE/13—Raw Copper, Sub-Committee NFE/13/2—Sampling and Analysis of Raw Copper.

CM(NFE) 6783—Draft B.S. Methods for the Analysis of Raw Copper—Silver and Tin.

Draft Specification prepared by Technical Committee ISE/18—Sampling and Analysis of Iron and Steel.

CM(ISE) 6903—Draft B.S.—Method for the Determination of Tin in Ferro-Tungsten and Tungsten Metal.

Book Reviews

CELLULOSE ACETATE PLASTICS. By VIVIAN STANNETT, Ph.D., F.R.I.C. Pp. xxiv + 325. London: Temple Press Ltd. Price 30s.

In the preface to this book it is claimed to be the first on its subject, yet cellulose acetate is the most versatile of plastics and is produced in tremendous quantities. Moreover, this material is by no means a recent introduction, although its use has markedly increased during the last twenty years or so. The author felt, therefore, that the time had come for a book on all aspects of cellulose acetate technology. The early history of this substance is controversial, but the author describes clearly the developments during the latter half of the nineteenth century and the industrial applications that followed. The book is designed to appeal to the average reader and small user, while stimulating the specialist; the writing is interesting and the author's objects should be achieved.

This addition to the numerous publications on plastics follows a common pattern. An account of the status of the industry, and of the raw materials upon which it is dependent, serves as an introduction to a description of the technology of cellulose acetate. The last-mentioned section forms the major part of the book and is accompanied by many illustrations of the specialised plant that is used. After the concluding chapter, entitled "Applications," there are three appendixes, *viz.*, "Table of Properties," "Chemical Tests" and "Trade Names." The analytical section does not give details of the methods included, but it will doubtless serve adequately the readers for whom the book is intended. In brief, this book gives a very good account of the plastic and its technology: the reviewer has no hesitation in recommending it.

G. H. WYATT

ORGANIC SYNTHESSES. Vol. 29. Edited by C. S. HAMILTON. Pp. 93 + index. New York: John Wiley & Sons Inc. London: Chapman & Hall, Ltd. 1949. Price 20s.

With nearly a thousand items to its credit, this well-established annual series of checked preparative methods might well be expected to have left for present treatment only some of the more obscure organic chemicals. On the contrary, we have here such relatively simple compounds as *p*-nitrobenzonitrile, protocatechuic and homophthalic acids, *tert*butylamine (by an alternative method to that in Vol. 27), methacrylamide, *m*-methoxybenzaldehyde, 2 : 6-dichlorophenol and 3-chloropropyl acetate. In any event, the starting materials are always available, either as commercial chemicals (at least, in America) or described elsewhere in the series. There are preparations for all tastes. The young dye-chemist can try 1-methylaminoanthraquinone and its 4-bromo-derivative; the acetylene worker 1-ethynylcyclohexanol; the ring-breaker 1 : 2 : 5-pentanetriol and 4-chlorobutyl benzoate; the heterocyclist indazole, 3-aminophthalhydrazide (luminol), trimethylene oxide, the cyclic sulphone of isoprene and 4-hydroxy-2-methylquinoline, while for the less ambitious there is oleyl alcohol by sodium reduction. In all, 34 preparations are described, some with intermediate stages; a few, *e.g.*, *m*-aminobenzaldehyde dimethylacetal and phthal*tert*butylimide are new compounds. In addition, some further varieties of Raney nickel, particularly effective for low-pressure hydrogenations, are described. Finally, a warning is issued against crystallising benzoyl peroxide from *hot* chloroform, as had been formerly recommended. The cumulative subject index covers volumes 20 to 29 inclusive.

Volumes 27, edited by R. L. Shriner, and 28, edited by H. Snyder, are also to hand and follow the general pattern. The analyst, as such, may be interested in 2 : 4 : 7-trinitrofluorenone

(Vol. 28) which forms stable complex compounds with a wide variety of aromatic compounds (*J. Amer. Chem. Soc.*, 1946, 1727; 1947, 1225), though less useful than picric acid or trinitrobenzene for naphthalene derivatives of low molecular weight. B. A. ELLIS

THE PHARMACEUTICAL INDUSTRY IN GERMANY DURING THE PERIOD 1939-45. British Intelligence Objectives Sub-Committee Surveys Report No. 24. Edited by J. B. M. COPPOCK. Pp. 120. London: H.M. Stationery Office. 1950. Price 3s. 6d. net.

This review of the German pharmaceutical industry, edited by Dr. J. B. M. Coppock, is the collaborative study of 28 main subjects covering the whole field of pharmaceutical research and manufacture and reported upon by specialist contributors. These surveys have been prepared from published reports in the B.I.O.S. series and include references to appropriate unpublished documents.

A considerable portion of the report is devoted to research into production of synthetic fine chemicals and isolates of medicinal value, but insecticides, rodenticides, antiseptics and disinfectants, amino-acids, protein hydrolysates and pharmaceutical preparations are also reviewed. Some diagrams and plates of tablet processing are given and eleven pages of references are included.

Although the subject-matter in each section is reported similarly, contributors have used their own individual styles and given their personal opinions on the value of the German work in their particular field; some full syntheses are given where interesting features are present. The writers are to be congratulated on transforming a documentary report into a readable description of the state of German pharmaceutical research during the war years.

The book gives little information of interest in the analytical field and throughout it is evident that scientific control was inadequate as judged by British standards. Further, the investigators found that little is to be learned of value in connection with pharmaceutical processing; in fact, apparently few new achievements have been effected compared with the state of knowledge before the war and technique appears to have been inferior to the methods used in this country.

However, much of the information given may still be of value to industry and it is presented in a convenient form for consultation. D. C. GARRATT

Publications Received

HETEROCYCLIC COMPOUNDS. VOLUME I. THREE-, FOUR-, FIVE- AND SIX-MEMBERED MONOCYCLIC COMPOUNDS CONTAINING ONE O, N AND S ATOM. Edited by R. C. ELDERFIELD. Pp. ix + 703. New York: John Wiley & Sons, Inc. London: Messrs. Chapman & Hall. 1950. Price 88s.

SYSTEMATIC ORGANIC CHEMISTRY. MODERN METHODS OF PREPARATION AND ESTIMATION. Fourth Edition. By W. M. CUMMING, O.B.E., D.Sc., F.R.I.C., M.I.Chem.E., F.R.S.E., I. VANCE HOPPER, Ph.D., A.R.C.Sc.I., F.R.I.C., and T. SHERLOCK WHEELER, D.Sc., F.R.C.Sc.I., F.R.I.C. Pp. xxviii + 556. London: Constable & Co., Ltd. 1950. Price 37s. 6d.

INORGANIC MICRO-ANALYSIS. By H. V. A. BRISCOE, D.Sc., A.R.C.S., F.R.I.C., and P. F. HOLT, B.Sc., Ph.D., D.I.C., F.R.I.C. Pp. vii + 171. London: Messrs. Edward Arnold & Co. 1950. Price 12s. 6d.

THE CONDENSED CHEMICAL DICTIONARY. Fourth Edition. Editorial Director: FRANCIS M. TURNER. Pp. xxix + 726. New York: Reinhold Publishing Corporation. London: Messrs. Chapman & Hall. 1950. Price 80s.

HANDBUCH DER ANALYTISCHEN CHEMIE. ELEMENTE DER SIEBENTEN HAUPTGRUPPE. TEIL III, BAND VII α . By W. FRESENIUS and G. JANDER. Pp. xiii + 245. Berlin: Springer-Verlag. 1950. Price DM 38.

CHEMICAL ANALYSIS. VOLUME 3. COLORIMETRIC DETERMINATION OF TRACES OF METALS. Second Edition. By E. B. SANDELL, Ph.D. Pp. xix + 673. New York and London: Interscience Publishers Inc. 1950. Price 72s.

Reports of the Analytical Methods Committee

THE Report of the Carotene Panel of the Sub-Committee on Vitamin Estimation, "The Determination of Carotene in Green Leaf Material: Part I, Fresh Grass," reprinted from *The Analyst*, November, 1950, 75, 568-576, is now available from the Editor; price to members 1s. 6d. and to non-members 2s. 6d.

HIS MAJESTY'S COLONIAL SERVICE
FEDERATION OF MALAYA

A VACANCY exists for a Research Officer (Forest Chemist) in the Forestry Department, Federation of Malaya. The duties of the post cover all aspects of wood chemistry but with special reference to the manufacture of paper pulp and fibre-board from mixed tropical hardwoods. The post is pensionable after three years' probation. The salary scale, including pensionable expatriation allowance, is \$490 per month to \$1065 per month (£686 per annum to £1491 per annum, current sterling equivalent at one Malayan dollar to 2/4d.) plus a variable cost of living allowance of 50% of basic salary subject to the following maxima:—for a single officer, \$150 per month (£210 per annum); for a married officer without children, \$300 per month (£420 per annum); for a married officer with children, \$375 per month (£525 per annum).

Government quarters, if available, are at a nominal rent and free first-class passages on first appointment and on leave are provided for the officer, his wife and children under 10 years, not exceeding four persons besides himself. A tour of service of three to four years earns approximately five months' paid leave in the United Kingdom. Income tax is at local rates which are very much lower than those in the United Kingdom. Candidates should preferably be under 30 and must possess an Honours degree in Chemistry and Associate membership of the Royal Institute of Chemistry. Preference will be given to candidates who have done post-graduate research in wood-chemistry or who have some experience in wood-pulp and fibre-board manufacture and some knowledge of forest products research in general. The selected candidate will be required to pass examinations in Malay Standard I, General Orders and Identification of Timbers in due course.

Write giving brief details of age, qualifications and experience to the Director of Recruitment (Colonial Service), Sanctuary Buildings, Great Smith Street, London, S.W.1, quoting reference No. 27106/45.

SOUTHERN RHODESIA GOVERNMENT

VACANCY: ANALYTICAL CHEMIST

A PPLICATIONS from men holding at least the B.Sc. degree in Chemistry are invited by the Government of Southern Rhodesia for appointment as an Assistant Analytical Chemist in the Government Analyst's Laboratory in Salisbury. The work of this Laboratory includes the analysis of waters, foods and drugs, dairy produce and certain clinical specimens; toxicology; forensic chemistry; and general miscellaneous analyses.

Salary scale will be £468 × £66 to £600 × £34 to £668 × £33 to £800 × £100 to £900 × £40 to £1140 per annum with efficiency barriers at the £668 and £800 per annum steps. If the successful applicant holds the M.Sc., A.R.I.C., or equivalent qualification the commencing salary on this scale will be £600 per annum. Consideration will also be given to granting a higher commencing salary in recognition of approved previous experience. In addition, existing regulations provide for the payment of a marriage allowance of £50 per annum to a married man who is maintaining his wife within the Colony, provided that salary plus marriage allowance does not exceed £850 per annum. A cost of living allowance, at present amounting to approximately 17 per cent. of salary will also be paid in terms of regulations.

The successful applicant will be required to pass a medical examination by a Southern Rhodesia Government Medical Officer, and will be provided with travelling fare from place of appointment to Southern Rhodesia for himself, and if applicable, half the cost of fares for his wife and any children under the age of eighteen years.

Application forms and further information from the Secretary to the High Commissioner for Southern Rhodesia, 429, Strand, London, W.C.2, to whom completed forms should be returned not later than the 30th January, 1951.

Canvassing will disqualify applicants.

LANCASHIRE COUNTY COUNCIL

SENIOR ASSISTANT ANALYST required for County Laboratory. The post will rank next to that of the Deputy County Analyst and applicants must possess the Fellowship of the Royal Institute of Chemistry Branch E.

Salary £685-£760 according to experience.

ASSISTANT ANALYST also required. Applicants should possess either a university degree or the A.R.I.C. and preferably had experience in the analysis of food and drugs.

Salary £450-£525 according to experience and qualifications.

Further particulars and application forms from County Medical Officer of Health, County Offices, Preston, to whom applications must be forwarded by 27th January, 1951.

ASSISTANT CHEMISTS required by a Major Oil Company for its London Laboratory handling a wide variety of problems affecting oils, greases and special petroleum products. Good education and Honours B.Sc. degree or A.R.I.C. are essential qualifications. Those appointed will be required to assist the Head of the Analytical Section in applying standard oil test methods and special analytical techniques to samples of new and used lubricants, engine deposits, etc. The vacancies carry opportunities for progress for young, energetic men, and in time may involve responsibility for the supervision of others. Salary will be commensurate with qualifications and experience; conditions of employment include pension and sickness benefit schemes. Applicants should write giving full particulars, quoting reference (Z. 1701) to Box 3762, THE ANALYST, 47, Gresham Street, London, E.C.2.

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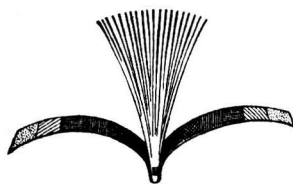
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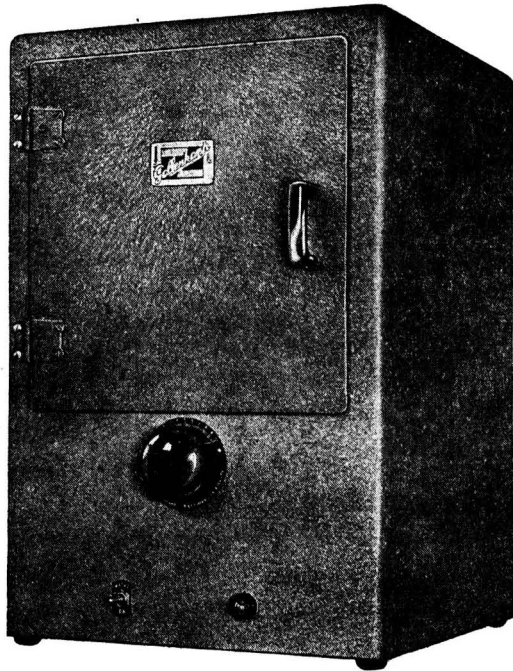
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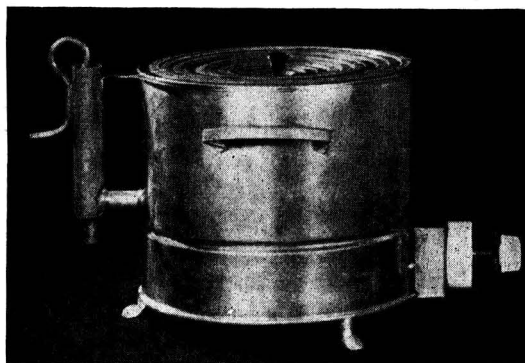
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