# THE ANALYST

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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, February 1st, 1950, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1. The chair was taken by the President, Mr. George Taylor, O.B.E., F.R.I.C.

The meeting was organised by the Physical Methods Group of the Society, and was devoted to "Modern Methods of Moisture Determination." The following papers were presented: "A Review of Some Developments in the Use of the Karl Fischer Reagent," by A. G. Jones, B.Sc., F.R.I.C.; "A Radio Frequency Moisture Meter for Routine Control," by A. T. S. Babb, B.Sc., A.R.I.C.; "Moisture Determination in Granulated, Pulverised or Milled Food Materials such as Sugar Products," by R. W. Money, M.Sc., F.R.I.C.; "The Determination of Moisture in Tobacco," by C. F. M. Fryd, B.Sc., A.R.C.S., A.R.I.C., and P. R. Kiff, B.Sc. A discussion followed.

# Method for the Estimation of Small Amounts of Carbon in Steel

BY K. GARDNER, W. J. ROWLAND AND H. THOMAS

SYNOPSIS—A brief survey is given of the methods available for the determination of small amounts of carbon (less than 0·03 per cent.) in steel. The method described utilises a combustion procedure in which the carbon dioxide produced is absorbed in baryta solution. The decrease in electrical conductivity of this solution is related to the carbon content. The difficulties which arise are discussed and necessary precautions are described. A device for the introduction of the sample into the combustion zone, without ingress of air, is shown. Adsorption of carbon dioxide by the pre-ignited boats is avoided by storing over soda-asbestos. A high efficiency of absorption in the baryta solution is attained by the use of a cell having a long absorption path and by addition of a non-ionic wetting agent, Lissapol N, to the absorbing solution. For steels containing less than 0·03 per cent. of carbon, the average deviation from the mean value does not exceed ±0·0005 per cent. The determination occupies 40 minutes, half the time needed for similar methods previously published. The apparatus can be constructed from laboratory equipment, and is robust and comparatively inexpensive. The method has been in satisfactory operation for over two years, and the results compare favourably with those obtained by the standard low-pressure method.

IN the course of an investigation in these laboratories, it was necessary to develop a method for the accurate determination of the carbon content of steel containing less than 0·03 per cent. of carbon. Three types of method were considered.

(*a*) *Classical microgravimetric procedures*—These have the disadvantages that a skilled operator is required and that the time for an estimation is long.

(*b*) *Low-pressure combustion method*—This method may be considered the standard procedure at the present time for the determination of carbon in low-carbon steels. The basic principles were devised by Yensen[1] in 1920. A system is evacuated and the sample of

steel then heated and ignited in purified oxygen. The carbon dioxide formed is collected in a liquid air trap and subsequently determined by expanding the gas into a known evacuated volume and observing the pressure. Improvements in the technique were made in the methods of Wooten and Guldner,[2] Murray and Ashley[3] and Murray and Niedrach.[4] In the method of Stanley and Yensen,[5] it is claimed that the average time for an estimation is 20 minutes and that an accuracy of ±0·0005 per cent. is obtained. Nesbitt and Henderson[6] use a modification of this method in which the steel is burned in a stream of purified oxygen and the evolved carbon dioxide collected in a special absorber containing caustic soda. The solution is then acidified and the volume of gas evolved is measured at low pressure.

All these methods have the disadvantage that the apparatus required is complicated and relatively expensive. Attention was, therefore, focussed on the third type of method.

(*c*) *Combustion of the sample in oxygen followed by absorption of the carbon dioxide in barium hydroxide solution*—The reduction in concentration of the barium hydroxide can then be measured, either by titrating the residual base with standard acid, as in Kalina and Joseph's method,[7] or by measuring the decrease in conductance of the solution. Cain and Maxwell[8] used the conductimetric method for the rapid determination of carbon with an accuracy of ±0·01 per cent. Bolliger and Treadwell[9] used a conductimetric method for the estimation of carbon in aluminium, the carbon dioxide being absorbed in caustic soda solution.

After much work had been carried out by the authors on this method, their attention was drawn to a reference in "Reports on the Progress of Applied Chemistry" to the work of Ericcson.[10] Using an absorption cell similar in design to that of Kalina and Joseph, he was able to determine carbon contents with an accuracy of ±0·0005 per cent. The average time for each analysis, however, was greater than 1 hour.

## Apparatus

A diagram of the apparatus is shown in Fig. 1. Oxygen is admitted from a cylinder, through the flow gauge A and thence is passed through sodium hydroxide B and sulphuric acid C. Carbon monoxide and hydrocarbons are converted to carbon dioxide and water by catalytic combustion of the gas in furnace D, which is packed with palladised asbestos and operated at 400° C. Any water and carbon dioxide formed are absorbed in U-tubes E and F, which contain anhydrous calcium chloride and soda-asbestos respectively. These are followed by a Pregl type bubble-counter G, containing sulphuric acid, which serves to indicate any leakage in the train. It is followed by a glass wool filter H and a 2-litre aspirator bottle J, which is connected to the combustion furnace by tap K. The aspirator provides a reservoir of oxygen for use during combustion of a sample. All joints between the purification furnace D and the combustion furnace are glass to glass, the rubber tubing merely acting as a seal. A mullite combustion tube, L (type triangle H5/T3411), is used, and after combustion the gases pass through a manganese dioxide tube M, which absorbs any sulphur dioxide formed. This tube is connected through rubber tubing and clip N to the absorption vessel P. Morgan Z8 combustion boats are used.

The entrance to the combustion tube is illustrated in Fig. 2. This part of the apparatus provides a gas-tight joint from the train to the furnace and at the same time minimises the volume of air introduced into the tube on insertion of the sample of steel. The steel cone R is fixed to the end of the tube by means of a ring of large-diameter heavy-section rubber tubing U. The steel cone is fitted to a B40 standard cone end-cap S, which is sealed at the extremity by glass tube V with rubber tubing. Extending to the narrow end of this end-cap is a steel tube T, which slides into the side-arm of the furnace tube. The sample boat W may be inserted into the position shown in the diagram, by removing the glass cone. Oxygen can then be passed through tube T until any atmospheric carbon dioxide is completely removed. The glass tube V can then be quickly removed and the boat pushed into the hot zone of the furnace tube with a steel rod, while oxygen passing out through T prevents admission of any air. The tube V is replaced and the combustion of the sample carried out.

The absorption vessel, details of which are shown in Fig. 3, was prepared by modifying a Friederich type absorption vessel (Pyrex catalogue type S31). The gas passes through the central spiral which contains the conductivity electrodes (A, A) and bubbles into the absorbent through a sintered-glass bubbler B. The bubbler was prepared by the method of Stone and Weiss[11] using 40 to 60 mesh Pyrex glass. The small gas bubbles produced follow a 26-inch path round the spiral and out through C. In order to measure the conductance, air is forced through a soda-asbestos tube into C by means of a rubber bulb, forcing the

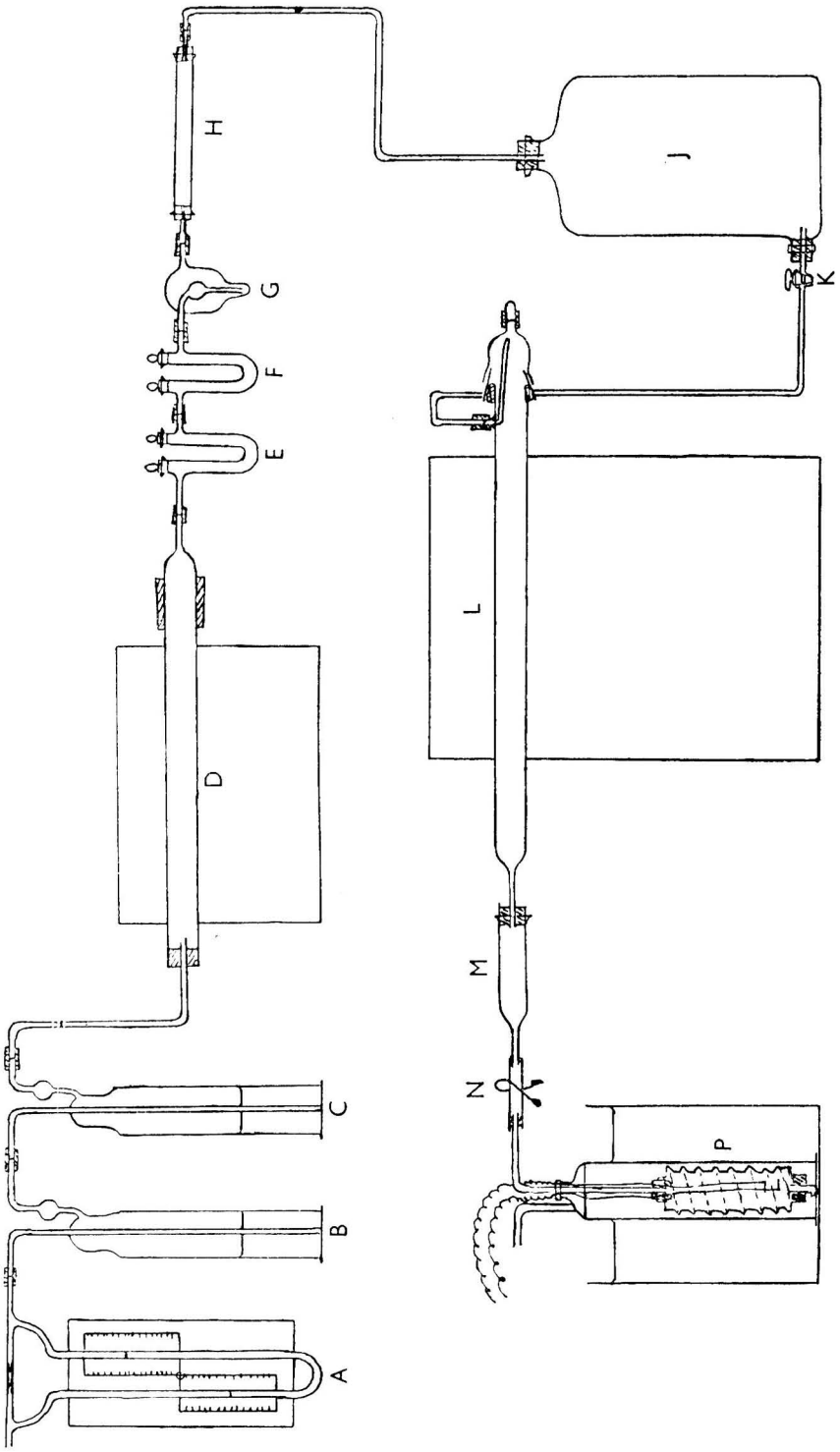


Fig. 1. Diagram of combustion apparatus

liquid back through the sinter into the measuring cell. Bubbles of purified air rising through the sinter serve to stir the liquid completely. The clip N is closed and the conductance measured with a Cambridge conductivity bridge. The cell is maintained at 20·0 ± 0·1° C. by means of a water-bath.

## Reagents

A suitable volume of reagent in the absorption vessel is 50 ml. In order to obtain a suitable range on the conductivity bridge, for steels containing about 0·03 per cent. of carbon, it is desirable to use a concentration of 1 g. of hydrated baryta, $Ba(OH)_2.8H_2O$, per litre. In addition, to ensure complete absorption, the absorbent contains 10 ml. of 2 per cent. v/v Lissapol N* solution per litre. The exact concentration of the baryta is not important. To facilitate delivery of a standard volume into the absorption vessel, the absorbent is stored in an aspirator bottle connected to an automatic pipette. The bottle is protected by a guard tube containing soda-asbestos.

## Procedure

Place 2 g. of the sample in a combustion boat and insert into the cool end of the combustion tube. Close the tube by means of the glass cone. Empty and dry the outer surfaces

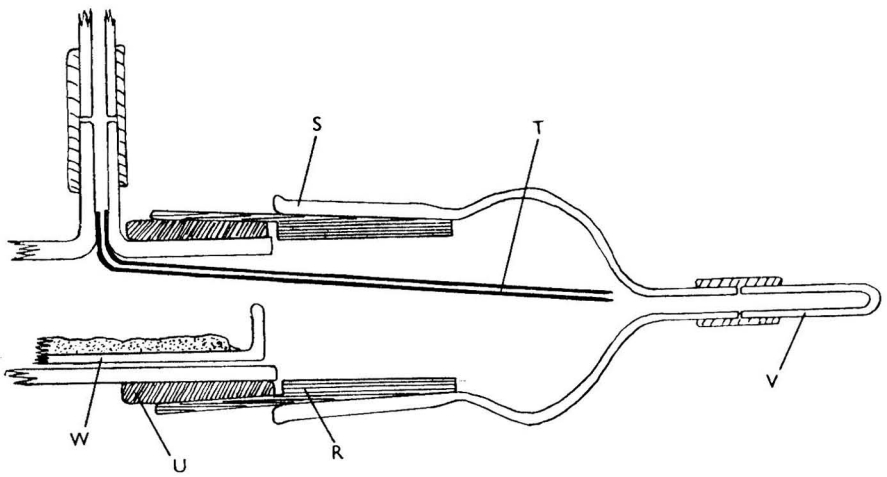


Fig. 2. Details of entrance to combustion tube

of the absorption vessel and blow purified air through the sinter to remove any liquid from the inside of the cell. Run in 50 ml. of baryta solution from the pipette. Connect the cell to the apparatus and pass oxygen through at a rate of 2·7 to 3·0 litres per hour. Adjust the temperature of the water-bath to 20 ± 0·1° C. and measure the conductivity at 5-minute intervals until the bridge reading is constant. Isolate the absorption vessel by means of clip N. Remove the stopper V from the end of the glass cone and push the boat into the hot zone of the furnace with a clean steel rod. The temperature of the furnace should be 1200° to 1250° C. Close the end of the cone and increase the oxygen flow to prevent the pressure in the apparatus falling unduly. If the sample consists of drillings, combustion will start almost immediately; with sheet samples there is a lag of about 1 minute. In both cases the time for burning a 2-g. sample is 2 to 3 minutes. During combustion the rate of oxygen flow increases to 7 to 10 litres per hour. When combustion is complete, as shown by a decrease in oxygen flow, open the clip which isolates the absorption cell and reduce the oxygen flow to 2·7 to 3·0 litres per hour. Determine the conductivity of the baryta solution after 15 minutes and thereafter at 5-minute intervals until the bridge reading is constant. With carbon contents of less than 0·01 per cent., a constant reading will be obtained in 20 minutes. With higher carbon contents 30 minutes is usually required.

The method of correlating the difference in bridge reading with carbon content is given below.

Barium carbonate may be removed, when necessary, from the sintered glass bubbler by means of dilute hydrochloric acid, followed by washing with water.

* Lissapol N is an ethylene oxide condensation product prepared by Imperial Chemical Industries Ltd.

## Experimental

The efficiency of the absorption was first checked with a known quantity of calcium carbonate as a carbon standard. This method proved successful for carbon contents greater than 0·02 per cent. For lower carbon contents it was difficult to weigh out the small amounts of calcium carbonate required and, therefore, sucrose was used. A standard solution of sucrose was made such that 1 ml. was equivalent to 0·4 mg. of carbon. Known volumes of this solution were delivered from a micro-burette either on to a porous boat lid or into a non-porous boat and these were placed inside an ordinary combustion boat. Water was removed, either by desiccating over phosphorus pentoxide or drying in an oven at approximately 90° C. These samples were then ignited as for a steel.

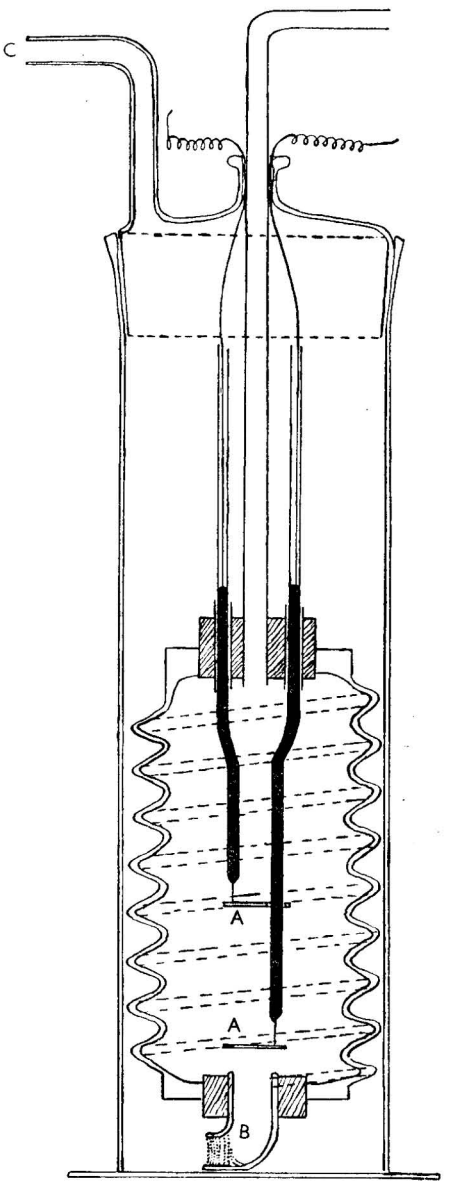

Fig. 3. Details of absorption vessel

The first experiments were carried out with an absorbent containing 1 g. of hydrated barium hydroxide per litre with no wetting agent. With gas flows below 2·5 litres per hour, the time for sweeping out carbon dioxide from the combustion tube was excessive.

When the flow was increased to 2·7 to 3·0 litres per hour, absorption was incomplete as shown in Fig. 4 (A) in which the difference in conductivity for this absorbent is plotted against carbon content. A theoretical curve for complete absorption is also shown, Fig. 4 (C). This theoretical curve was constructed from data relating conductance and concentration obtained from Gmelin's Handbook[12] and the "Handbook of Chemistry and Physics."[13] These data were checked by measuring the conductance of baryta solutions of known concentrations, the cell constant being determined by measurement of standard potassium chloride solutions.

The absorption was increased by the introduction of butyl alcohol into the absorption reagent, and by doubling the concentration of barium hydroxide, but was still incomplete. Finally, a non-ionic surface-active agent, Lissapol N, was incorporated in the reagent. The relation between conductivity difference for this solution and percentage carbon is shown in Fig. 4 (B). It is seen that for carbon contents below 0·03 per cent., the difference between this curve and the theoretical curve does not exceed 0·0005 per cent. of carbon. It was considered that curve B, Fig. 4, was sufficiently close to the theoretical curve to warrant its use as a calibration curve for the method.

Fig. 5 shows the percentage absorption of the two reagents as a function of carbon concentration. With carbon contents greater than 0·03 per cent., the absorption falls off rapidly.

Owing to the small amount of carbon estimated, care had to be taken in the preparation of the samples of steel, *e.g.*, all surface grease had to be carefully excluded and samples were never touched by hand after preliminary cleaning by abrasion.

It was found that if the combustion furnace was switched off and allowed access to the air, a considerable period (2 to 3 hours) was required, on re-heating, to attain a steady reading on the conductivity bridge. This was probably due to carbon dioxide adsorption on the walls

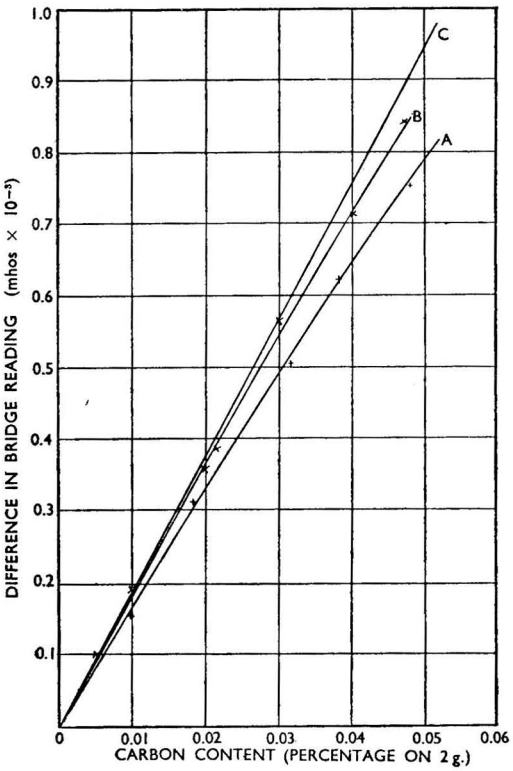


Fig. 4. Relationship between carbon content and conductivity difference. Curve A, solution containing 1 g. of $Ba(OH)_2.8H_2O$ per litre. Curve B, solution containing 1 g. of $Ba(OH)_2.8H_2O$ plus 0·2 ml. of Lissapol N per litre. Curve C, theoretical relationship

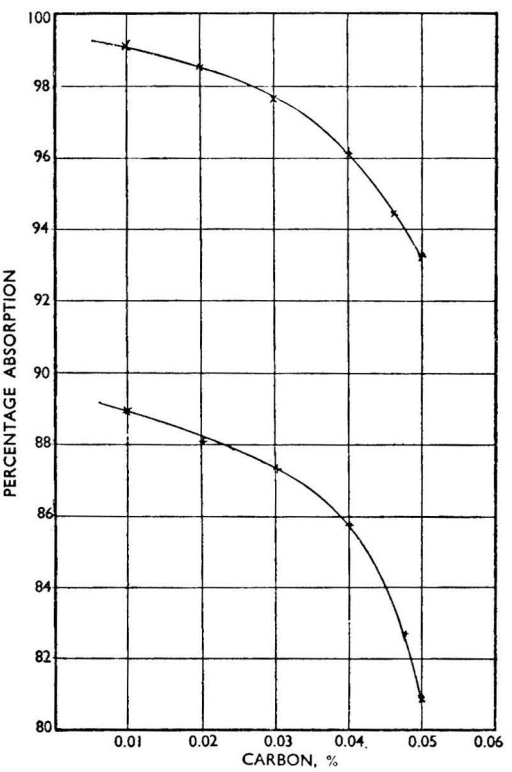


Fig. 5. Effect of carbon content on absorption. Lower curve, solution containing 1 g. of $Ba(OH)_2.8H_2O$ per litre. Upper curve, solution containing 1 g. of $Ba(OH)_2.8H_2O$ plus 0·2 ml. of Lissapol N per litre

## Table I

### Determination of carbon content of B.C.S. carbon steels

| B.C.S. Steel No. | Weight of sample, g. | Carbon expressed on basis of assumed 2-g. sample: Calculated, % | Carbon expressed on basis of assumed 2-g. sample: Found, % |
|---|---|---|---|
| | No wetting agent | | |
| 218 | 0·1200 | 0·0092 | 0·0090 |
| | 0·2087 | 0·0161 | 0·0155 |
| | 0·2377 | 0·0183 | 0·0185 |
| 156 | 0·2147 | 0·0245 | 0·0245 |
| | 0·2626 | 0·0300 | 0·0292 |
| 213 | 0·2264 | 0·0414 | 0·0412 |
| 158 | 0·2289 | 0·0531 | 0·0535 |
| | 0·02 per cent. of Lissapol N present | | |
| 218 | 0·2010 | 0·0155 | 0·0160 |
| 156 | 0·2045 | 0·0234 | 0·0230 |
| 213 | 0·2062 | 0·0377 | 0·0380 |
| 158 | 0·2010 | 0·0467 | 0·0470 |

of the combustion tube. During routine analysis, this difficulty was avoided by maintaining the combustion furnace overnight at a temperature of 700° to 800° C., while passing a very slow trickle of oxygen through the apparatus.

The combustion boats had to be ignited in oxygen before use and stored in a desiccator over soda-asbestos. It was found that, if the boats were exposed to the air for an appreciable time after ignition, a blank of 0·01 mg. of carbon (0·0005 per cent. on a 2-g. sample) was obtained.

Because of the difficulty in obtaining low-carbon standard steels, a number of determinations were carried out on small weights of B.C.S. carbon steels. The results are shown in Table I.

Table II shows the results of ten analyses on a sample of commercial low-carbon steel. These results show the expected deviation caused by heterogeneity of the steel. The average deviation from the mean is very close to the value obtained by Stanley and Yenson,[5] who analysed a similar steel by the low-pressure combustion method.

TABLE II

CARBON CONTENT OF A COMMERCIAL LOW-CARBON STEEL

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Carbon, % .. | 0·0067 | 0·0070 | 0·0080 | 0·0072 | 0·0070 | 0·0067 | 0·0075 | 0·0075 | 0·0077 | 0·0080 |

Mean 0·0073 ± 0·0004(1)%

Duplicate determinations were carried out on a standardised sample of low-carbon steel which had been analysed by the low-pressure combustion method. The results were as follows—

| | Carbon, % |
|---|---|
| Low-pressure method .. .. .. .. | 0·0060 ± 0·0005 |
| Conductimetric method .. .. .. | 0·0065 |
| | 0·0062 |

SUMMARY

With this conductimetric method for the determination of carbon in low-carbon steels, containing less than 0·03 per cent. of carbon, the average deviation from the mean value does not exceed ±0·0005 per cent. The determination occupies about 40 minutes, about half the time needed for similar methods previously published. The apparatus can be constructed from laboratory equipment and is robust and comparatively inexpensive. This method has been in satisfactory operation in these laboratories for over two years.

The authors are indebted to the Director of the Nelson Research Laboratories for permission to publish this work.

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*September*, 1949

# The Determination of Residual Chlorine in Water

By G. U. HOUGHTON

(*Read at the meeting of the Society on Wednesday, November 2nd, 1949*)

Synopsis—The introduction of break-point chlorination created a need for tests which would distinguish between free and combined residual chlorine. A satisfactory method for the determination of residual chlorine must be highly sensitive, tolerably free from interference from traces of other oxidants and able to give sharp differentiation between free chlorine and chloramines.

A review is given of the methods available, including several methods, both colorimetric and amperometric, based on the original acid tolidine method of Ellms and Hauser, and methods using *p*-amino-dimethylaniline, methyl orange or neutral *o*-tolidine, and an iodimetric method for higher chlorine contents.

The large-scale chlorination of water has now been practised for over 40 years, so that the measurement of small amounts (under 1 p.p.m.) of residual chlorine has long been a matter of considerable technical importance. It is therefore rather remarkable that prior to the second world war very few methods of measuring residual chlorine had been put forward and, indeed, the well-known *o*-tolidine method has, until quite recently, been unchallenged. However, in 1939 the whole subject received considerable impetus from the discovery, or rather the re-discovery, of the break-point effect in the chlorination process.* The recognition of the importance of this effect by Faber[3] and a little later by Griffin[4] and Calvert[5] created a need for simple control tests which would distinguish between free and combined residual chlorine. It also directed attention to the reactions which take place between hypochlorite and ammonia at high dilution. By this time too, it had become widely appreciated that chloramines are far less potent germicides than free hypochlorous acid. The ideal requirement nowadays is therefore a method which is at once sensitive, free from interference by traces of other oxidants and able to give sharp differentiation between free chlorine and chloramine; it should also preferably be sufficiently simple to serve as a waterworks control test.

The more important of the tests that have been used for residual chlorine and some of the recent advances that have been made in the methods for its determination are as follows.

## The *o*-tolidine colorimetric method—

This method was devised by Ellms and Hauser[6] as far back as 1913 and has the great merit of simplicity combined with high sensitivity: unfortunately, however, other oxidants interfere, notably ferric iron, nitrite and oxidised manganese.

Owing to the difficulty of preparing reliable standards from chlorine water or hypochlorite it has always been the custom to match the *o*-tolidine - chlorine colours against permanent standards prepared from dichromate or against colour-glasses. The standards employed have been those originally given by Ellms and Hauser, but it has long been realised that they are not entirely satisfactory, the main difficulty being that they are only strictly applicable at a cell depth of 300 mm.

The Ellms and Hauser method has been studied exhaustively in the past and various procedures have been proposed whereby the effect of interfering oxidants may be overcome. Nevertheless, in view of the great importance of the *o*-tolidine method it has recently been reviewed by the Control of Chlorination Committee of the American Waterworks Association, whose recommendations were incorporated in the 1946 edition of "Standard Methods for the Examination of Water and Sewage" (p. 92).

The method recommended by the American Committee was based mainly on the thorough studies of the *o*-tolidine method made earlier by Chamberlain and Glass.[7] The method put

* The Dutch workers, Holwerda in 1928[1] and Ruys as early as 1914[2] had demonstrated the phenomenon, but it is fair to say that it was the intensive studies of the American workers in 1939 and 1940 that opened up a new chapter in chlorination practice.

forward by these workers, which was subsequently adopted, differs from the earlier American standard method in the following important particulars—

(1) The use of a greater proportion of tolidine in the final colour mixture.
(2) The use of a more acid reagent, so that the final pH of the solution lies between 0·3 and 1·3 and there is consequently less interference from iron and nitrite and also more rapid colour-formation.
(3) The addition of the sample to the reagent instead of *vice versa*.
(4) The permanent standards proposed are a modification of those worked out by Scott and are buffered chromate solutions, without any addition of copper sulphate. They have the great merit that for chlorine contents up to 1·0 p.p.m. the cell depth employed is immaterial.

In addition to the advantages mentioned above, Chamberlain and Glass state that the procedure gives increased stability of colour and that Beer's law is obeyed up to 1·5 p.p.m. of chlorine and deviations therefrom are at a uniform rate between 1·5 and 10 p.p.m. Manganese, however, still interferes. It must also be noted that with the more strongly acid reagent and quicker colour development, the "flash" and "arsenite - tolidine" methods, *vide infra*, become far more difficult to apply.

THE *o*-TOLIDINE "FLASH" TEST—

It has long been known that chloramines produce colour with acid *o*-tolidine reagent much more slowly than does free chlorine. In 1940, Laux[8] used this fact as the basis of a qualitative test for free chlorine. The sample is rapidly mixed with *o*-tolidine reagent and the rate of colour development observed. Any delay in colour development is taken to indicate the presence of chloramine. The test is very rough, but on account of its simplicity has been much used, particularly in swimming-bath control, and it is accepted as standard in the United States. Oxidised manganese interferes by giving a "flash" colour with tolidine and the rate of colour development is dependent on temperature.

*o*-TOLIDINE - ARSENITE METHOD—

This rather ingenious method, which was first put forward by Hallinan[9] in 1944, is a means of distinguishing between free and combined residual chlorine, but it also permits a correction to be made for interfering substances. Use is made of the fact that under the prescribed experimental conditions arsenite can reduce both chlorine and chloramines but not nitrite or oxidised iron or manganese. Free chlorine is therefore measured by adding arsenite immediately after the tolidine, so as to reduce any chloramine before it has time to produce colour. Simultaneously, colorimetric evaluations are made for total residual chlorine and interfering oxidants (*viz.*, without arsenite) and for interfering oxidants only (*viz.*, by adding arsenite before tolidine). The amount of total, free and combined chlorine can then be ascertained by difference. Although this method does not give very clear-cut differentiation of the free chlorine and has certain pitfalls, it has proved very useful. It is seriously affected by temperature, and traces of bromide cause difficulty by accelerating the production of colour by the chloramine.

AMPEROMETRIC TITRATION METHOD—

This review would not be complete without brief reference to the amperometric method of determining residual chlorine first described by Marks and Glass[10] in 1942. As far as is known this method has not been used in this country except for research purposes, but it is of great promise. The procedure consists in titrating the chlorine with sodium arsenite in neutral solution, the end-point being observed amperometrically using a gold or platinum cathode and a silver anode in 2 *M* potassium chloride. Under these conditions the iron, manganese and nitrite do not oxidise the arsenite and do not interfere. A first titration is made which gives the free chlorine: potassium iodide is then added to "activate" the chloramine which may then be determined by a second titration. The outstanding merits of this method are its freedom from interference by manganic compounds and high precision: it was claimed by Marks and Glass that amounts of chlorine up to 10 p.p.m. could be determined to within 0·01 p.p.m.

*p*-AMINO-DIMETHYLANILINE (P.A.D.A.) METHOD—

A number of workers[11,12,13,14] have investigated the use of this substance as a reagent for available chlorine, with which it gives a red coloration. Moore[15] found that at pH 6·0

the reaction was obtained with free chlorine only and that it was necessary to lower the pH to 4·0 to obtain a coloration with chloramines: on this fact he based a qualitative and semi-quantitative method. Palin[16] placed the reactions on a more rigidly quantitative basis by matching the red colour against that produced by running a standard iodine solution into a control tube containing buffer and reagent; reaction of the chloramine was obtained by subsequent addition of potassium iodide.

Manganese interferes somewhat in the amino-dimethylaniline method but, as when using *o*-tolidine, the interfering colour may be allowed for by its measurement after reduction of the chlorine with arsenite. Copper also interferes but may be inhibited by using hexa-metaphosphate in the buffer solution. A comparator fitted with colour standards from 0·1 to 2·0 p.p.m. of chlorine has now been developed for use with this reagent in the control of swimming-pool chlorination.

METHYL ORANGE METHOD FOR FREE CHLORINE—

In hydrochloric acid solution (pH 3), free chlorine bleaches methyl orange but chloramine is without immediate effect. This was the basis of a volumetric method for the determination of free chlorine advanced by Holwerda[1] in 1928. Quite recently Taras has again investigated this method and has put forward a colorimetric[17] and a micro-titration[18] procedure using methyl orange. These methods are of considerable interest and appear to be worthy of further study and trial.

NEUTRAL *o*-TOLIDINE METHOD—

If in the *o*-tolidine test the reagent is of low acid concentration (*e.g.*, 5 ml. of 20 per cent. v/v hydrochloric acid per litre) only free chlorine will produce a colour, the pH of the test solution being too high to effect hydrolysis of the chloramines. The "neutral" tolidine test, which depended on this fact, was proposed by Laux and Nickel[19] in 1942. In their test the colour produced was blue with samples of pH below about 7·9 but yellow or orange at higher pH values. This colour difference was a serious drawback, as also was the fact that the colour was somewhat affected by the *o*-tolidine/chlorine ratio, besides fading rapidly.

Palin[20] has recently re-examined the neutral *o*-tolidine test and used the reagent in a novel method of chlorine determination. In this new method the tolidine is used at pH 5 to 6, in the presence of metaphosphate and with an *o*-tolidine/chlorine ratio of 6/1. Under these conditions free chlorine produces a pure, stable, blue colour which, provided the residuum does not exceed 4 p.p.m., can be matched against standard glasses; the higher residual chlorine may be titrated with ferrous ammonium sulphate. Further, after addition of potassium iodide, monochloramine may be made to give a blue colour with the reagent and likewise be titrated or matched. Chlorine testing kits (one of them photo-electric) which make use of the Palin neutral *o*-tolidine method are on the market.

In studies using this method, Palin observed that with certain chlorinated waters the results obtained for total residual chlorine were decidedly lower than the corresponding iodimetric figures. Moreover, it appeared that in these waters a chloramine was present which could not react with iodide to give the colour reaction unless the solution was first acidified and then brought back to neutrality with bicarbonate. This discovery was in line with an observation made many years previously by Harold[21] that unless acid was present in the iodimetric titration, all the chloramine would not react with iodide. This phenomenon was attributed by Harold to the presence of dichloramine. From detailed investigations, Palin has likewise concluded that in his neutral tolidine method the first fraction of the chloramine, activated by iodide, is monochloramine, while the second, which is not so activated unless previously hydrolysed, is dichloramine.

Nitrogen trichloride may also be produced during break-point chlorination and by a further extension of the Palin method, it too may be determined. For this purpose the solution is tested again after prior extraction with carbon tetrachloride, the nitrogen trichloride present being calculated from the difference between the "free chlorine" values before and after extraction. It is thus possible to draw up a balance sheet showing the proportions of free chlorine and mono-, di- and tri-chloramines in the total residual content. Unfortunately, any oxidised manganese present interferes, even under the practically neutral conditions, but may be allowed for by its measurement after adding arsenite to reduce the chlorine. Iron and nitrite are without effect.

It would seem that these studies by Palin are most important. Not only are they valuable from the point of view of analytical control but, applied in this way, the neutral

*o*-tolidine method should be useful for research purposes, *e.g.*, for the study of possible differences in the germicidal efficiency of the three chloramines. Incidentally, they also show that it is not safe to regard as chloramine only that part of the chlorine residuum which reacts after the so-called "activation" by iodide. Such an assumption was made by Marks and Glass and, indeed, by Palin himself in his earlier work using amino-dimethylaniline. The mechanism by which iodide induces the reaction of monochloramine with tolidine is uncertain; it may depend on intermediate liberation of iodine and this is a point which might repay investigation. In an analogous way bromide promotes the reaction of tolidine and chloramine in acid solution.

In the Palin (neutral tolidine) method any nitrogen trichloride reacts as free chlorine. The formation of this compound during break-point chlorination has been recognised by several workers (*e.g.*, Holwerda[1] and Marks and Glass[10]), but there is apparently little information as to its germicidal value. A feature of Palin's results is that they give a simple method of measuring the content of trichloride and they show that surprisingly large amounts may be present. The possibility that nitrogen trichloride would react as free chlorine in the amino-dimethylaniline and arsenite - tolidine tests must also be borne in mind.

IODIMETRIC METHOD—

In general, this method is useful for chlorine residua over 1 p.p.m., provided nitrite and manganese are absent and ferric iron does not exceed 2 p.p.m. The thiosulphate used is conveniently 0·0025 *N* and a 500-ml. or 1000-ml. sample may be used, but in the past the advisability of standardising the thiosulphate under similar conditions has usually been ignored. The iodimetric method suggested by the Joint British Water Analysis Committee therefore requires the thiosulphate to be standardised against iodine liberated from iodate at high dilution. It should also be stressed that since, as mentioned earlier, dichloramine does not appear to react with iodide in neutral solution, the sample should always be acidified with sulphuric acid before iodimetric titration.

APPROVED BRITISH METHODS FOR THE DETERMINATION OF RESIDUAL CHLORINE—

The British Committee that has been considering methods of water analysis soon found that the prescription of an approved method for residual chlorine would be one of its most difficult tasks. The shortcomings of the Ellms and Hauser *o*-tolidine method were realised, but the Committee had to bear in mind the effect of any changes on the validity of the residual chlorine testing kits which are in use at waterworks and swimming-baths throughout the country. It was recognised that any change should only be undertaken after full discussion with all parties concerned. It accordingly recommended that the existing Ellms and Hauser method and standards be approved *pro tem.* but that a new and wider Committee should be convened to go into the whole question.

The position was complicated by the fact that while the Committee was sitting, the new (1946) American standard methods for residual chlorine were laid down. Much time and trouble have obviously been devoted to the new American methods, but it was agreed that further study was necessary before they could be recommended forthwith as the basis on which British testing kits could be manufactured. The Committee were also impressed by the fact that the whole subject of residual chlorine determination was in a somewhat fluid condition and that new and apparently improved methods were still being introduced.

In the preparation of this survey I have received a number of useful suggestions from Dr. A. T. Palin, and to him my grateful acknowledgment is due.

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## Discussion

Mr. R. F. Milton drew attention to a completely new method for the estimation of residual chlorine. He said that this was the first time that a direct method for the determination of chlorine had been put forward, all the existing methods being based on oxidation potential and not directly on the presence of chlorine. For this reason they were not specific.

A short description of this method had been published[1]; briefly, it depended on the fact that when free chlorine was brought into contact with the cyanide ion, cyanogen chloride was produced quantitatively. The cyanogen chloride was then allowed to react with pyridine to form a quarternary derivative which, when coupled with an aromatic amine, produced an intense colour which could be made the basis of a quantitative estimation.

This method would also detect free bromine, but otherwise was entirely specific for free chlorine.

Mr. Milton felt that the method was worth further investigation. The high concentration of pyridine, 5 per cent., was a disadvantage, but it might be possible to use other organic compounds such as nicotinic acid.

Dr. Houghton replied that he had made a few trials of the method described by Mr. Milton, working on 5-ml. quantities of water. He could confirm the high sensitivity of the method, but he had found difficulty with the benzidine precipitating. He thought the method showed promise, however, and was of considerable interest.

Dr. H. Liebmann said that he had tried Mr. Milton's recently published method, and could also confirm its high sensitivity. However, this sensitivity appeared to vary in accordance with the concentration of the residual free chlorine, decreasing very markedly at higher concentrations as determined in distilled water by amperometric titration. Above about 4 p.p.m. of free chlorine, further increase produced only a very slight increase in colour density.

He had also obtained some evidence that at least a part of the chloramine is estimated in addition to free, available chlorine by Milton's method. These experiments, however, had been carried out on highly polluted water, with which all methods for the determination of free chlorine became rather uncertain.

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# The Estimation of Chitin and Chitin Nitrogen in Crawfish Waste and Derived Products

By Miss M. M. BLACK and H. M. SCHWARTZ

Synopsis—The determination of chitin and chitin nitrogen in crawfish waste and derived products has been subjected to a critical study. In the proposed method, chitin is isolated and either weighed as such or, in the case of the determination of chitin nitrogen, its nitrogen content is determined by one of the standard methods.

When applied to crude chitin samples, the precision of the proposed method is of the order of 0·5 per cent. of the mean. It is somewhat lower (±3 per cent. of the mean) in the case of crawfish meals.

The method is similar to the A.O.A.C. method for the determination of crude fibre. A comparison of the results obtained on a number of crawfish meals by the two methods shows close agreement.

The chitin, chitin nitrogen and total nitrogen content of a number of crawfish meals are reported, and the importance of making a correction for chitin nitrogen when calculating the protein content of such meals is stressed.

Approximately 9000 tons of waste are available annually from the production of canned and frozen crawfish tails on the west coast of the Union of South Africa and South-West Africa. At present only a limited proportion of the waste is converted into crawfish meal, which is used for poultry feed. An investigation into the possibility of producing chitin on a commercial scale from crawfish waste was undertaken by the authors. The results of this work will be published elsewhere. As part of this investigation the determination of chitin in crawfish waste and products derived from it was studied. The estimation of chitin nitrogen in crawfish meals used for feeding purposes was also studied. This is of interest because it is customary to sell the meal on the basis of its protein content, which is calculated from the total nitrogen content. Since chitin contains 6·90 per cent. of nitrogen, and since it is very doubtful whether this is available to animals, with the possible exception of ruminants, it is desirable to subtract the chitin nitrogen from the total nitrogen when calculating the protein content of crawfish meal.

A survey of the literature revealed that the methods most commonly used for the estimation of chitin in plant and animal tissues are based on the isolation of chitin.[1,2,3] Crustacean shells are usually treated first with excess of hydrochloric acid to dissolve out the mineral matter. The sample is then subjected to repeated treatments with 4 to 10 per cent. aqueous sodium or potassium hydroxide. The residue is finally decolorised with dilute potassium permanganate and extracted with alcohol and ether. No attempt appears to have been made to determine the number of alkali treatments necessary to remove completely all non-chitinous material, or the extent to which repeated alkali digestions cause de-acetylation and subsequent loss of chitin. Chitin has also been determined by conversion to de-acetylated chitin (chitosan) by the action of very concentrated potassium hydroxide at 120° to 150° C., and then weighed as such.[4] This method is unsatisfactory, however, since the amount of chitosan obtained varies inversely with the duration of the alkali treatment.[3]

## Experimental

In the present method, chitin is extracted and weighed as such. The following procedure was finally adopted.

*Estimation of chitin*—Weigh 0·2 to 0·4 g. of crude chitin or 2 g. of crawfish waste or meal into a 250-ml. beaker, add 50 ml. of *N* hydrochloric acid and heat on a boiling water-bath for 1 hour. At the end of this period, filter the contents of the beaker through a sintered glass crucible (porosity G1) or a piece of linen. Wash the beaker and the filter with boiling water until the washings are no longer acid. Then wash the residue on the filter back into the beaker with 100 ml. of 5 per cent. w/v sodium hydroxide solution, and digest on a steam-bath for 1 hour. The residue at this stage should consist of chitin together with any silica

present in the sample. Filter it through an alundum crucible or through a Gooch crucible prepared with ignited asbestos,[5] wash thoroughly with boiling water and finally wash twice with about 15 ml. of acetone. Dry the crucible and contents at 110° C. to constant weight. Incinerate the contents of the crucible in an electric muffle-furnace or over a Meker burner at a dull red heat until all carbonaceous matter is consumed. Cool the crucible and re-weigh. Report the loss in weight as chitin.

*Estimation of chitin nitrogen*—Carry out the acid and alkali digestions as described above. Filter the residue left after the alkali digestion through a sintered-glass crucible or through a piece of linen, and wash thoroughly with hot water. Transfer the chitin to a 250-ml. Kjeldahl flask, using the least possible amount of water. Evaporate the water to less than 5 ml., taking care to avoid bumping. Add 25 ml. of concentrated sulphuric acid and 10 g. of potassium sulphate (0·25 g. of copper selenite or any other catalyst may also be added if desired) and complete the nitrogen determination in the usual way.[6]

## Results

### Number of alkali treatments required—

Previous workers have used at least three alkali treatments to purify their chitin in the estimation of chitin in both animal and plant materials.[1,2,3] The number of alkali treatments necessary to ensure the removal of all non-chitinous organic matter was investigated. The isolation of chitin from crawfish meal samples was carried out by the recommended procedure. The residue after the first alkali digestion was dried and weighed and then subjected to a

Table I

Effect of successive treatments with 100 ml. of 5 per cent. NaOH on the weight of the residue before ignition

| Weight of residue after | | | Loss in weight* | |
|---|---|---|---|---|
| 1st treatment, g. | 2nd treatment, g. | 3rd treatment, g. | 2nd treatment, % | 3rd treatment, % |
| 0·2749 | 0·2701 | 0·2660 | 1·8 | 3·2 |
| 0·2410 | 0·2369 | 0·2327 | 1·7 | 3·5 |
| 0·2554 | 0·2508 | 0·2459 | 1·8 | 3·7 |
| 0·2074 | 0·2054 | 0·2030 | 1·0 | 2·1 |
| 0·2543 | 0·2507 | 0·2501 | 1·4 | 1·7 |
| 0·2992 | 0·2946 | 0·2916 | 1·4 | 2·4 |
| 0·2542 | 0·2499 | 0·2489 | 1·7 | 2·1 |

* As percentage of weight of residue after 1st alkali treatment.

Table II

De-acetylation of chitin under conditions of estimation

| No. of alkali treatments | Weight of chitin isolated, g. | Weight after acetic acid treatment, g. | De-acetylated chitin, % |
|---|---|---|---|
| 1 | 0·1821 | 0·1817 | 0·2 |
| 1 | 0·1843 | 0·1834 | 0·5 |
| 1 | 0·2532 | 0·2522 | 0·4 |
| 1 | 0·2660 | 0·2639 | 0·8 |
| 3 | 0·2660 | 0·2651 | 0·3 |
| 3 | 0·2327 | 0·2313 | 0·6 |
| 3 | 0·2459 | 0·2451 | 0·3 |

second and finally a third treatment with 100 ml. of 5 per cent. sodium hydroxide solution. The results are summarised in Table I. It will be seen that the second and third alkali treatments cause small losses in the weight of the residue obtained after the first treatment. These losses, however, are only of the order of 2 to 4 per cent. of the weight of the chitin in the sample. This is of the order of experimental error of the method, and consequently one treatment with alkali is deemed sufficient in the estimation of chitin in crawfish meals and

derived products. That one alkali treatment suffices to remove all but a trace of non-chitinous organic matter was further demonstrated by the fact that fish meals, which were known not to have been admixed with crawfish meal, gave less than 0·2 per cent. of residue when treated according to the proposed method (Table III (*a*)).

The de-acetylation of chitin even after three treatments with 5 per cent. sodium hydroxide solution under the conditions employed in the determination is negligible. This was demonstrated by heating samples of chitin isolated by the proposed method with 3 per cent. v/v acetic acid on a steam-bath for 1 hour. Under these conditions de-acetylated chitin dissolves readily. The loss in weight of the chitin preparations, however, was less than 1 per cent. (Table II).

The chitin isolated from crawfish wastes by the proposed method was pure white in colour. Most of the colour was removed by the alkali treatment and what remained was taken out by washing with acetone. Further decolorisation with dilute potassium permanganate as employed by other workers is thus unnecessary for products derived from crawfish waste.

PRECISION OF METHOD—

The recovery of chitin added to fish meals was studied. Pure chitin was prepared from crawfish shells by treatment with hydrochloric acid, followed by repeated treatment with 5 per cent. sodium hydroxide. Any de-acetylated chitin produced in the process was removed by treatment with 3 per cent. acetic acid. The purified chitin was added to samples of pilchard meal which had been shown to contain less than 0·2 per cent. of chitin. Determination of the chitin content of the mixtures by the proposed method gave recoveries of 98·2 to 100·1 per cent. (Table III).

TABLE III

RECOVERY OF PURIFIED CHITIN ADDED TO FISH MEALS

(*a*) BLANK DETERMINATIONS ON PILCHARD MEALS

| Sample | Weight of meal taken, g. | Weight of chitin isolated, g. | % |
|---|---|---|---|
| 1 | 2·0402 | 0·0000 | nil |
| | 2·0690 | 0·0001 | nil |
| 2 | 2·1369 | 0·0023 | 0·11 |
| | 1·9300 | 0·0026 | 0·13 |

(*b*) RECOVERY OF ADDED CHITIN

| Pilchard meal used | Weight of pilchard meal taken, g. | Chitin in pilchard meal, g. | Purified chitin added, g. | Chitin found, g. | Recovery, % |
|---|---|---|---|---|---|
| 1 | 2·2344 | nil | 0·2015 | 0·2018 | 100·1 |
| | 1·9917 | nil | 0·2081 | 0·2070 | 99·5 |
| 2 | 2·7097 | 0·0032 | 0·3354 | 0·3330 | 98·4 |
| | 2·0703 | 0·0024 | 0·4316 | 0·4270 | 98·3 |
| | 2·7022 | 0·0032 | 0·1969 | 0·1964 | 98·2 |
| | 2·2167 | 0·0027 | 0·2644 | 0·2639 | 98·7 |

Determination of the chitin content of thirteen samples of crude chitin, containing 60 per cent. or more of chitin, was carried out in duplicate by the method described. The difference between duplicate determinations ranged from 0·2 to 1·6 per cent. of the mean. The average deviation from the mean was 0·4 per cent. When the method was applied to crawfish meals, the agreement between replicate determinations was not so close. Duplicate, and in some cases quadruplicate, determinations were carried out on thirteen samples of crawfish meal from various sources. The deviation of a single determination from the mean for the sample ranged from 0·2 to 10·7 per cent. The average deviation from the mean was 3·0 per cent. One reason for the lower precision of the method when applied to crawfish meals appears to be the difficulty of sampling the meal properly, even after it has been finely ground. This was particularly noticeable when the meal contained a high proportion of sand.

The precision of the method for the determination of chitin nitrogen in meals is of the same order as that for the determination of chitin. The determination of the chitin nitrogen content of nine crawfish meals was carried out in duplicate. The difference between duplicates ranged from 1·4 to 9·1 per cent. of the mean. The average deviation from the mean was 1·8 per cent.

COMPARISON OF THE METHOD WITH THE A.O.A.C. METHOD FOR THE DETERMINATION OF CRUDE FIBRE—

The method described here for the determination of chitin is very similar in principle to the A.O.A.C. method for the determination of crude fibre.[5] A comparison of the values obtained by the two methods for a number of crawfish meals is given in Table IV. The results in each case refer to the dry, fat-free meal. The values obtained by the two methods

TABLE IV

COMPARISON OF VALUES FOR CHITIN AND CRUDE FIBRE (A.O.A.C. METHOD) IN CRAWFISH MEALS

| Meal sample | Chitin, % | Crude fibre, % |
|---|---|---|
| 3 | 11·4 | 11·7 |
| 4 | 9·4 | 10·5 |
| 5 | 11·2 | 11·6 |
| 6 | 10·5 | 10·2 |
| 7 | 13·1 | 13·1 |
| 8 | 11·5 | 11·8 |
| 9 | 13·8 | 15·4 |

are in very close agreement, except in two cases (samples 4 and 9), and here the differences are within the limits of the experimental errors of the methods. The A.O.A.C. method for crude fibre determination may therefore be used to determine chitin in crawfish products. The method described here is preferred, however, since it requires less rigid adherence to specified conditions.

THE CHITIN AND CHITIN NITROGEN CONTENT OF CRAWFISH MEALS—

The chitin, chitin nitrogen and total nitrogen content of nine crawfish meals are recorded in Table V. The chitin nitrogen content as determined by the proposed method is generally

TABLE V

CHITIN, CHITIN NITROGEN AND TOTAL NITROGEN CONTENT OF CRAWFISH MEALS

| Chitin, % | Chitin nitrogen, % (Calc.) | Chitin nitrogen, % (Found) | Total nitrogen, % | Chitin nitrogen/total nitrogen, % |
|---|---|---|---|---|
| 13·1 | 0·91 | 0·75 | 7·06 | 10·7 |
| 12·1 | 0·84 | 0·86 | 6·29 | 13·6 |
| 11·4 | 0·79 | 0·73 | 7·70 | 9·5 |
| 11·2 | 0·77 | 0·68 | 9·79 | 7·0 |
| 10·5 | 0·73 | 0·82 | 9·20 | 8·9 |
| 13·1 | 0·90 | 0·81 | 7·37 | 11·1 |
| 11·5 | 0·79 | 0·76 | 9·12 | 8·3 |
| 13·8 | 0·96 | 0·94 | 8·16 | 11·6 |
| 13·6 | 0·94 | 0·94 | 7·91 | 11·9 |

slightly lower than that calculated from the chitin content of the meal, using the theoretical value of 6·90 per cent. for the nitrogen content of chitin. This is to be expected, since even carefully purified chitin samples generally contain less than the theoretical amount of nitrogen.[1]

In the meals examined, the chitin nitrogen ranged from 7·0 to 13·6 per cent. of the total nitrogen in the meal. The importance of making a correction for chitin nitrogen in calculating the protein content of crawfish meals is therefore apparent.

We are indebted to the South African Council for Scientific and Industrial Research for permission to publish this work. We are also indebted to the Fishing Industries Research Institute, Cape Town, for supplying a number of crawfish meals used in this work.

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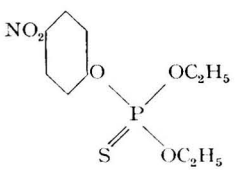
# The Analysis of *p*-Nitrophenyl Diethyl Thiophosphate, E605, Parathion

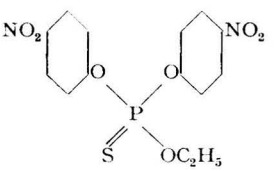
BY J. C. GAGE

SYNOPSIS—The high toxicity of the insecticidal compound generally known as parathion or E605 has necessitated a sensitive method for its determination in the atmosphere or in edible crops. A method is described in which the compound in toluene solution is reduced to the corresponding amino compound, which is extracted into acid, diazotised and coupled with N-sulphatoethyl-*m*-toluidine. The coefficient of variation of a solution containing 5 μg. per ml. is of the order of 2 per cent.; the lower limit of sensitivity for the analysis of plant tissues depends upon the blank value for the material.

THE historical development and chemical synthesis of the organic phosphorus insecticides have been discussed at a recent symposium of the Association of Applied Biologists.[1] One of these compounds, *p*-nitrophenyl diethyl thiophosphate (I), has been shown to be highly effective against a wide range of insect pests; it was synthesised in Germany and given the code reference E605, and in America the U.S. Department of Agriculture has used the official name "parathion." It is being manufactured in this country and both names are in current use; more recently the tendency, which will be followed in this communication, is to use the term parathion.




(I)

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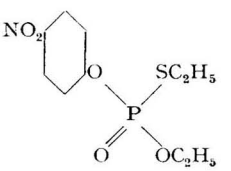


(III)

Analytical methods for determining parathion are not only necessary to control the strength of the crude commercial product, and of insecticidal dusts and solutions made therefrom, but also, on account of the high mammalian toxicity of the compound, to determine the concentration in the atmosphere during its manufacture and use. Moreover, if edible crops have been treated with such an insecticide, it may be desirable to know the residual amount of parathion present in the crop after harvesting.

It is possible to base a colorimetric method on the hydrolysis of parathion to nitrophenol, which takes place readily in alkaline solution. Such a method is not, however, sufficiently sensitive for the determination of parathion in the atmosphere or in plant tissues. Averell and Norris[2] have described a sensitive method which has been used to estimate the residual amount in a variety of plant materials; the tissues are extracted with benzene, which is then evaporated to dryness after treatment with an adsorbent to remove pigments. The residue is dissolved in aqueous alcohol and after reduction of the nitro group to an amino group with zinc dust and hydrochloric acid, an azo dye is developed by diazotisation and coupling with N-(1-naphthylethylenediamine) after removal of excess of nitrite with ammonium

sulphamate. In the method described in this paper, reduction is effected by heating a toluene solution, which may be a plant tissue extract or the absorbing liquid from a suitable air sampler, with zinc dust and acetic acid under refluxing conditions; the reduced parathion is then extracted from the toluene with dilute hydrochloric acid. The advantage of this procedure is that evaporation of the solvent is avoided and, as plant pigments are not extracted from the organic liquid into the aqueous phase, there may be no necessity for their removal. In the development of the azo dye it has been found advantageous to couple with N-β-sulphatoethyl-*m*-toluidine,[3] which is more readily available and more stable than the reagent used by Averell and Norris,[2] and does not require the addition of ammonium sulphamate; it is, however, necessary to neutralise the hydrochloric acid and part of the extracted acetic acid to facilitate coupling, and the addition of alcohol gives greater stability to the colour.

## Method

The following procedure was designed for the estimation of atmospheric contamination or of residual parathion in plant material, in which only a few micrograms are present. If larger amounts can be taken for analysis, suitable modifications may be made if desired.

### Reagents—

*Toluene*—Ten parts of commercial redistilled toluene shaken with 1 part of concentrated sulphuric acid for 2 hours and washed free from acid.*

*Glacial acetic acid*—Analytical reagent quality.

*Zinc dust*—Commercial zinc metal dust.

*Hydrochloric acid, 0·5 N.*

*Concentrated hydrochloric acid*—Analytical reagent quality.

*Sodium hydroxide solution,* 10 per cent.—Ten grams of sodium hydroxide of analytical reagent quality dissolved and made up to 100 ml. with distilled water.

*N-β-sulphatoethyl-*m*-toluidine,* 1 per cent.—One gram of the pure commercial product dissolved and made up to 100 ml. with distilled water. It should be stored in an amber bottle and discarded when the solution turns pink.

*Sodium nitrite solution,* 0·25 per cent.—Freshly prepared each week from a 5 per cent. stock solution of sodium nitrite (analytical reagent quality) kept in a refrigerator.

*Ethanol*—95 per cent.

### Reduction of the nitro group—

Approximately 15 ml. of the toluene solution, containing not more than 7 μg. per ml. of parathion, is introduced into a 6 × 1 inch test tube fitted with a 30-cm. air condenser by means of a ground glass joint. To this is added 0·25 ml. of glacial acetic acid and 0·25 g. of zinc dust. The tube is then placed in an oil-bath at 130° to 140° C. and the contents heated under reflux for 15 minutes. After cooling, the zinc is allowed to settle and 10 ml. of the clear solution are transferred to a stoppered 6 × $\frac{5}{8}$ inch test tube, and shaken for 3 minutes with 2·5 ml. of 0·5 *N* hydrochloric acid. After separation of the layers, 2 ml. of the aqueous layer are removed by a pipette to a tube graduated at 5 ml.

### Development of the azo colour—

Add 0·2 ml. of 0·25 per cent. sodium nitrite solution, mix and allow to stand for 15 minutes. Add 0·4 ml. of 1 per cent. N-sulphatoethyl-*m*-toluidine followed by 0·6 ml. of 10 per cent. sodium hydroxide solution; mix and allow to stand for 15 minutes. Add 3 drops of concentrated hydrochloric acid and 1 ml. of 95 per cent. ethanol and make up to 5 ml. with distilled water.

### Colour measurement—

For this investigation the Unicam D.G. spectrophotometer has been used with 0·5-inch diameter tubes and the azo colour read at 510 mμ. With the Spekker absorptiometer, Ilford filter No. 604 is suitable. The colour may be read immediately after making up to volume and is stable for several hours.

* Some supplies of toluene were not amenable to this treatment. It has since been found that the B.D.H. sulphur-free grade is satisfactory without acid treatment.

A standard curve relating optical density to concentration is constructed from toluene solutions containing known amounts of parathion and submitted to the above procedure, the colours being read against a blank from toluene similarly treated. For all determinations a toluene blank is employed; when plant material is investigated the toluene is first shaken with similar material that has not been treated with parathion.

DISCUSSION—

The method is specific for compounds that can be reduced to an amino compound capable of forming an azo dye. Amines may be excluded by acidifying the initial aqueous solution or washing the toluene solution with acid. *p*-Nitrophenol, which occurs in small quantity in commercial parathion, does not interfere, but *bis*-*p*-nitrophenyl ethyl thiophosphate (II), which is present as up to 10 per cent. of the crude product, does give a colour. Some difficulty has been experienced in obtaining a pure sample of parathion as a reference; many of the so-called pure samples obtained by distillation are grossly contaminated by an isomer (III), which is produced if parathion is heated above 140° C.[4] Methods of analysis for these impurities are being elaborated and will be the subject of a later communication.

Twelve determinations on a toluene solution containing 5 μg. per ml. gave a mean optical density 0·590 with a standard deviation of 0·010 and a coefficient of variation of less than 2 per cent. In the analysis of plant tissues the lower limit of sensitivity is largely controlled by the blank value, the apparent parathion content of the untreated material; the optical density obtained with this blank may be of the order of 0·05.

The method has been used satisfactorily to analyse the atmosphere during the manufacture of parathion insecticides, a sample of air being passed through toluene in a gas bubbler. An investigation of the residual parathion in a variety of plant materials is at present in progress; the results will be reported in detail later.

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# Spot-tests for the Identification of Alloying Elements in Copper-Base Alloys*

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SYNOPSIS—The tests described in this paper constitute a complete qualitative scheme for the non-destructive examination of copper and its alloys. The elements that can be detected are: manganese, zinc, tin, iron, lead, silicon, nickel, aluminium, beryllium, arsenic, cadmium, cobalt, chromium and phosphorus. The tests consist of addition of drops of reagent to the cleaned metal surface, followed by further reagent to produce a coloured precipitate characteristic of the metal sought, or removal of the drop of solution from the metal surface on to a filter-paper or spot-plate, for production of a specific reaction. The aim has been to reduce to a minimum the number of operations and the manipulative skill required so that the tests can be applied with satisfactory results by persons of limited chemical knowledge.

THE tests to be described in this paper constitute the last of a series of researches dealing with the detection of alloying elements in various types of alloys. Papers already published for the spot-testing of alloys include, "Steels,"[1] "Aluminium and Magnesium-base Alloys,"[2] "Zinc-base Alloys,"[3] "Lead-base Alloys"[4] and "Tin-base Alloys."[5] As far as possible these tests have been employed in the present series.

* Communication from the Armament Research Establishment (formerly Research Department, Woolwich).

*Apparatus*—It has not been found necessary to introduce any new apparatus and, since adequate description has already been given in previous papers, no further words need be added here.

THE TESTS—

Copper offers a very wide range of alloying elements, and tests have been evolved for the following elements: manganese, zinc, tin, iron, lead, silicon, nickel, aluminium, beryllium, arsenic, cadmium, cobalt, chromium and phosphorus. The usual alloying quantities of selenium, tellurium and silver are so small that no definite tests have been forthcoming; hence these elements are not included in the present work. The test to be described for silicon is based on dye-absorption by the hydrated silica; the preliminary results were so perplexing that an investigation was carried out, by one of us, to determine the exact condition under which absorption occurred. The findings of this investigation have been adapted to the test for silicon, but a more detailed account will be published at some future date by the author concerned. It has been found possible to test for aluminium and beryllium at the same time in such a way that both elements can be detected by their distinctive markings. After a single-wash treatment, to bleach the aluminium completely, the beryllium can be plainly seen.

Our aim, as before, has been to make every test specific and unambiguous. Compositions of the trial alloys are given in the Appendix, pp. 199–200, and the numbers at the end of each test refer to that Appendix.

It is very important to the success of the tests that the surface of the specimen should be thoroughly cleaned with a fine emery paper, Grade IG or similar, immediately before the reagents are applied.

### (I) MANGANESE

*Reagents*—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Sodium bismuthate (solid).

*Method*—Place 3 drops of (*a*) on the cleaned surface and leave for 5 minutes, add a further 2 drops and transfer, with the aid of a capillary tube, to the well of a white spot-plate. Drop into the solution a little of (*b*), stir and leave for the full development of colour. In presence of more than 15 per cent. of manganese, rapid decomposition into the hydrated oxide occurs; between 0·4 per cent. and 15 per cent. of manganese is indicated by varying intensities of purple permanganic acid, and 0·1 per cent. is visible as a light purplish coloration of the drop. In absence of manganese the drop remains blue.

Tried on: Samples Nos. 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12*—Manganese present; all results positive.

Nos, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22—Manganese absent and all results negative.

### (II) ZINC

*Reagents*—(*a*) Concentrated nitric acid (sp.gr. 1·42).
(*b*) Distilled water.
(*c*) Sodium hydroxide solution (20 per cent.).
(*d*) Diphenylcarbazone (1·5 per cent. solution in alcohol).
(*e*) Ammonium nitrate solution (20 per cent.).

*Method*—Place 1 drop of (*a*) on the cleaned surface and leave until the vigorous attack has subsided, then wash off with a fine jet of distilled water on to a clean watch-glass. Add 3 drops of (*c*) and stir thoroughly; the mixture should now react alkaline to litmus paper. Filter off the cupric hydroxide precipitate through a glass-tube filter, collecting the filtrate on a 12·5-cm. Whatman No. 541 filter-paper, supported on the open mouth of a beaker. Wash the watch-glass with 3 drops of (*b*) and pour through the filter-tube. Remove the tube, place the filter-paper on a clean tile and cover with a second filter-paper thoroughly soaked with (*e*); ensure complete contact at all points by rolling with a glass rod. After 20 to 30 seconds, strip off the ammonium nitrate paper, replace the test paper on its beaker and leave exposed to air for 5 to 10 minutes. At the end of this period the filter-paper ought to be free from all "fixed" alkali and substantially free from ammonia. Add 4 drops of (*d*), followed when

* First discovered by spot-tests and subsequently confirmed by chemical analysis.

spreading is complete by a further 4 drops. Again transfer to the tile and re-treat with a filter-paper well soaked in (*e*); this time manipulate the glass rod from the outer edges of the coloured spot to prevent undue spreading of the colours and to ensure an ample excess of ammonium nitrate all over the coloured patch. Remove the upper paper and suspend the test-paper to dry.

When more than 3 per cent. of zinc is present, the first addition of reagent (*d*) to the slightly ammoniacal test-paper results in a deep violet patch, whilst 1 per cent. of zinc gives a violet ring just inside the outer edge of the reagent patch, the remainder being orange-red in colour. In absence of zinc, or where the zinc content is low, the coloured ring is usually reddish-brown. Final treatment with (*e*) tends to accentuate the zinc colour whilst changing the reagent - ammonium nitrate colour from reddish-brown to brown. When dry, all papers not containing zinc show a peach-coloured centre with a brownish outer ring; 0·5 to 2·0 per cent. of zinc gives a peach centre more or less completely flecked with violet and a rather broad violet ring, or band, at the outer edge. Above 3 per cent. of zinc gives a deep violet colour to the whole reagent patch.

If the zinc content is less than 1 per cent., the above test should be replaced by the following.

Treat a 12·5-cm. Whatman No. 541 filter-paper with 2 or 3 ml. of an equal mixture of (*d*) and (*e*) and leave to dry; the paper should then appear very pale mauve with a yellow outer band. Filter the alkaline mixture, obtained as described above, on to this pre-treated paper. Remove the tube, wash the paper, from the centre, with 2 drops and then with 3 drops of (*e*), and finally treat with a disc of filter-paper moistened with (*e*) and hang up to dry. The zinc should now appear as a broadish irregular purple-violet band about 2 to 3 inches in diameter.

Tried on: Samples Nos. 17, 23, 24, 25, 26, 27, 21, 28, 16, 22, 1, 29, 30, 31, 32, 33, 34, 35, 36—Zinc present; all results positive.

Nos. 13, 14, 4, 37, 40, 41, 19, 45, 12, 15, 5, 42, 43—Zinc absent and all results negative.

### (III) Tin

*Reagents*—(*a*) Concentrated nitric acid (sp.gr. 1·42), 1 vol.; tartaric acid solution (50 per cent.), 1 vol.

(*b*) Potassium iodide solution (20 per cent.).

(*c*) Concentrated hydrochloric acid (sp.gr. 1·16), 1 vol.; potassium cobalticyanide solution (10 per cent.), 5 vols.

(*d*) Toluene-3 : 4-dithiol[6] solution in acetone (0·5 per cent.), 2 vols.; thioglycollic acid solution in acetone (0·5 per cent.), 1 vol.

*Method*—Attack the surface of the cleaned specimen with 1 drop of (*a*) and leave to react for 5 minutes. Add 2 drops of (*b*), stir well, spread out the drop and leave until the iodine colour has disappeared. Add 6 drops of (*c*), stir thoroughly, then remove about half the volume of the liquid, by means of a capillary tube, and drop on the centre of a 12·5-cm. filter-paper. When the liquid has finished spreading, add 4 drops of (*d*) to the centre of the cobalticyanide precipitate. In presence of tin, a yellowish band moves outwards until spreading ceases, then transformation occurs and the yellow ring turns red from the outer edge; for tin contents above 1 per cent., the whole of the area bounded by the ring also appears red. In absence of tin the paper remains white.

*Notes on Method*—The transferred precipitate should be light buff or greenish-blue in colour. The transformation, or development time, varies somewhat for different percentages of tin, *e.g.*, more than 0·3 per cent. of tin gives a colour almost immediately, 0·3 to 0·1 per cent. takes about 1 minute to give a colour and less than 0·1 per cent. may take 3 or 4 minutes; full development of the colour takes place within 5 minutes of addition of the "dithiol" reagent.

Tried on: Samples Nos. 44, 22, 21, 46, 47, 48, 49, 50, 51, 52,* 53,* 1*—Tin present; all results positive.

Nos. 6, 40, 19, 4, 37, 16, 15, 54, 55, 14, 13, 56, 11, 42, 36, 34, 35, 57—Tin less than 0·06 per cent. and all results negative.

* First discovered by spot-tests and subsequently confirmed by chemical analysis.

### (IV) Iron

*Reagents*—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Potassium cyanide solution (20 per cent.), 2 vols.; sodium hydroxide solution (20 per cent.), 1 vol.
(*c*) Ammonium nitrate solution (5 per cent.).
(*d*) Ammonium thiocyanate solution (10 per cent.), 2 vols; hydrochloric acid (sp.gr. 1·16), 1 vol.

*Method*—Add 2 drops of (*a*) to the cleaned surface and allow to react for 3 or 4 minutes. Transfer the drops of acid to the well of a glazed porcelain spot-plate, add 6 drops of mixture (*b*), stir well until all the blue copper hydroxide has been converted to double cyanide, and add more reagent (*b*) if necessary to complete the solution of hydroxide. Specimens containing neither iron nor manganese give a water-white solution, nickel in large amounts imparts a yellow colour, and high tin contents result in formation of a white precipitate. Iron gives a brown precipitate of ferric hydroxide, often no more than a brown coloration for contents below about 0·1 per cent.; however, coagulation occurs on standing, and a slight precipitate may be seen. Manganese, when present, gives a dark brownish-black precipitate, completely masking any iron that may be present; hence further treatment is necessary to distinguish the iron. Transfer the dark brownish manganese precipitate to the centre of a No. 541 filter-paper (or any filter-paper that *does not* give an iron reaction with thiocyanate), and wash 3 or 4 times with 1-drop washings of (*c*). To the washed precipitate add 2 drops of (*d*); a red coloration develops in presence of iron, but if manganese alone is present, it merely dissolves in the acid leaving the paper white.

Tried on: Samples Nos. 15, 11, 1, 6, 58, 59, 49, 21, 32, 51, 50, 48, 10,* 35,* 5,* 27,* 4*—Iron present; all results positive.

Nos. 40, 25, 28, 37, 22, 42, 45, 44—Iron absent and all results negative.

### (V) Lead

*Reagents*—(*a*) Concentrated nitric acid (sp.gr. 1·42), 1 vol.; tartaric acid solution (50 per cent.), 1 vol.
(*b*) Distilled water.
(*c*) Sodium chromate solution (5 per cent. in water).

*Method*—To the surface of the cleaned specimen add 2 drops of (*a*), leave until the reaction appears to be completed, then add 3 drops of (*b*) followed by 2 drops of (*c*), stir well and leave for a few seconds. Transfer the drop and precipitate, if any, by means of a capillary tube, to the centre of a close-grained filter-paper in such a manner that each drop is allowed to spread completely before the next drop is added; finally, wash twice with 3 drops of (*b*). In presence of lead, a yellow patch is visible at the centre of the paper; when wet, the paper usually has an outer yellow band of excess reagent, but this is completely reduced to tervalent chromium during the drying process. In absence of lead, or for lead contents below about 0·15 per cent., the paper is exactly as described above but without a central yellow patch.

Tried on: Samples Nos. 21, 48, 51, 49—Lead present; all results positive.
Nos. 50, 22, 11, 17, 20, 19, 15, 6, 45, 44, 14, 13, 16, 1, 52, 42, 40—Lead less than 0·16 per cent. and all results negative.

### (VI) Silicon

*Reagents*—(*a*) Concentrated nitric acid (sp.gr. 1·42), 1 vol.; syrupy phosphoric acid (sp.gr. 1·75), 1 vol.
(*b*) Distilled water.
(*c*) Ammonium chloride solution (saturated).
(*d*) Rhodamine B solution[7] (0·05 per cent. in water).
(*e*) Ammonium chloride solution (5 per cent.), 1 vol.; hydrochloric acid solution (5 per cent.), 1 vol.

*Method*—Add 2 drops of (*a*) to the cleaned surface and leave to react for at least 5 minutes, add 3 drops of (*b*), stir, then tilt the specimen and allow the drops to fall on to a clean watch-glass, scraping the surface of the specimen to remove any adhering particles. Add 4 drops of (*c*), stir, and follow with 4 drops of (*d*), stir again thoroughly and leave for 5 minutes for

* Iron first found by spot-tests and subsequently confirmed by chemical analysis.

precipitation and absorption to be completed. Transfer the reaction solution, by means of a capillary tube, dropwise on to the centre of a filter-paper, supported on the open mouth of a beaker. Wash by dropping 2 drops of (*c*) on to the centre from near the surface of the paper; repeat twice with 2-drop washings and finally with 3 or 4 1-drop washings of (*e*); the last washing treatment clears out any precipitated reagent leaving the centre quite clear in the absence of silicon. The presence of silicon is indicated by the formation of a deep magenta-coloured absorption precipitate, which dries to a light magenta spot against a pale pink background. The papers when dried can be kept indefinitely. It has been found that when cobalt is present, as well as silicon, there is a tendency towards formation of a black matrix, which is quite insoluble in all acid mixtures except those containing hydrofluoric acid. Our reluctance to employ such a dangerous acid compels us, for once, to accept a test which is not quite specific, but which has never been known to fail in *absence* of cobalt. In presence of cobalt, a black precipitate without other indications of silicon would suggest that silicon may be a constituent of the alloy.

Tried on: Samples Nos. 60, 35, 61, 62, 63, 64, 65, 66,* 67,* 75,* 76,* 77,* 78, 79—Silicon present; all results positive.

Nos. 40, 49, 6, 19, 51, 11, 22, 50, 68—Silicon less than 0·1 per cent. and all results negative.

### (VII) Nickel

*Reagents*—(*a*) Brominated hydrochloric acid (sp.gr. 1·20).
(*b*) Diluted ammonia solution (1 + 1), 3 vols.; ammonium phosphate solution (10 per cent.), 1 vol.
(*c*) Alcoholic dimethylglyoxime solution (saturated).
(*d*) Diluted ammonia solution (1 + 9).

*Method*—Attack the cleaned surface with 1 drop of (*a*) and leave until the bromine colour has been dispelled. Add 2 drops of (*b*), or sufficient to make the drop alkaline (test with a fragment of litmus paper), stir, then follow with 4 or 5 drops of (*c*) and stir again. The nickel glyoxime precipitate can be plainly seen from as little as 0·5 per cent. of nickel; however, it is better, as a matter of routine, to transfer the drops to the centre of a filter-disc and to wash three or four times with (*d*); by this procedure a slight dirty pink precipitate can be obtained from nickel contents down to 0·08 per cent. The background colour of the paper is a light greenish-yellow with an outer emerald-green edge. In absence of nickel, the centre of the paper is free from coloured precipitate.

Tried on: Samples Nos. 56, 42, 43, 69, 70, 71, 59, 11, 54, 72, 57, 58, 74, 19, 73, 39, 34, 21, 48—Nickel present; all results positive.

Nos. 33, 15, 16, 1, 36, 22, 13, 14, 51, 52—Nickel absent and all results negative.

### (VIII) Aluminium and beryllium

*Reagents*—(*a*) Brominated hydrochloric acid (sp.gr. 1·16).
(*b*) Sodium hydroxide solution (20 per cent.), 1 vol.; potassium cyanide solution (10 per cent.), 2 vols.
(*c*) Sodium hydroxide solution (5 per cent.).
(*d*) Ammonium chloride solution (20 per cent.).
(*e*) Ammonium chloride solution (20 per cent.), 1 vol.; ammonium citrate solution (50 per cent.), 1 vol.
(*f*) Ammonium aurine tricarboxylate solution (0·1 per cent. in alcohol).
(*g*) Ammonium citrate solution (50 per cent.).

*Preparation of reagent paper*—Pipette 1 ml. of reagent (*f*) on to a 12·5-cm. filter-paper (preferably No. 541), causing the liquid to spread as evenly as possible whilst attempting to concentrate the reagent into a wet patch approximately 8 to 9 cm. in diameter; dry over a source of hot air.

*Method*—Place 1 drop of (*a*) on the cleaned surface and leave to react for 5 minutes. Add 4 to 5 drops of (*b*), stir well until the original white precipitate has dissolved; the solution should now be alkaline and quite clear, except in presence of iron when a brownish-black

* Only black cobalt-silicide (?) was visible.

precipitate will be observed. Transfer the alkaline solution dropwise to the centre of a prepared reagent paper supported on the open mouth of a beaker.

ALUMINIUM—

Transfer the filter-paper to a white glazed tile, moisten a 9-cm. filter-disc with reagent (*d*), place flat on the wet patch of the reagent paper and ensure thorough contact by rolling a glass rod over the papers. Remove the upper ammonium chloride paper, discard, replace the reagent paper on its beaker and leave for 1 minute. In absence of both aluminium and beryllium the paper becomes perfectly white. Aluminium is indicated by a *broad* band of scarlet, approximately 1·5 to 2·5 inches in diameter, the inner edge being slightly irregular and slightly paler in colour. Beryllium, when present with aluminium, is indicated by a *narrow irregular ring*, always just inside the inner edge of the aluminium band and of a more intense scarlet colour; the remainder of the paper is white.

BERYLLIUM—

To confirm the presence of beryllium, repeat the test but, after the transferred liquid has finished spreading, treat with 2 drops of (*c*), which causes the beryllium ring to become twisted into a scalloped pattern. Transfer to a glazed tile, soak a 9-cm. filter-disc with mixture (*e*), place over the reagent paper and ensure thorough contact at all points by rolling with a glass rod; leave for 1 minute, remove the chloride - citrate paper and discard. Place the reagent paper on its beaker and wash once with (*g*) by allowing the liquid to flow readily from a capillary tube whilst describing a circle, just inside the coloured area. The broad band due to aluminium is completely bleached by this treatment and, after about 5 minutes, the paper is completely white in absence of beryllium. Beryllium is indicated by a narrow irregular reddish-scarlet ring, the colour of which seems to be enhanced by the ammonium citrate treatment; the aluminium colour remains bleached even when the paper is dry.

Tried on: Samples Nos. 11, 36, 34, 6, 54, 80, 81, 73, 59, 58, 82, 83, 84, 56—Aluminium present; all results positive.
Nos. 1, 19, 45, 16, 17, 22, 15, 12, 14, 13, 10—Aluminium absent and all results negative.
Nos. 38, 55, 66, 68, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95—Beryllium present; all results positive.
Nos. 11, 36, 34, 6, 54, 80, 81, 73, 59, 58, 82, 83, 84, 56—Beryllium absent and all results negative.

*Note*—In all instances of aluminium and beryllium being present together, both reactions were clearly visible.

## (IX) ARSENIC

*Reagents*—(*a*) Diluted nitric acid (sp.gr. 1·20), 1 vol.; potassium ferricyanide solution (10 per cent.), 1 vol.
(*b*) Diluted sulphuric acid (1 + 3).
(*c*) Mercuric chloride solution (saturated).
(*d*) Zinc metal (arsenic-free and previously treated as detailed below).

(i) *Preparation of reagent paper*—Soak a filter-paper in reagent (*c*), hang up to drain off excess of the reagent, and allow to dry; brush off loose crystals of mercuric chloride and cut the paper into small strips of approximately 1·5 × 0·25 inches.

(ii) *Preparation of metallic zinc*—Boil small lumps of granulated zinc in a 1 per cent. solution of cadmium sulphate for a few minutes, remove and wash the zinc, and store under distilled water until required for the test.

*Method*—Place 4 drops of (*a*) on the cleaned surface, the liquid being spread out *immediately*, as far as possible, with a pointed glass rod. Leave to react for a few seconds until it turns semi-solid, and then immediately scrape off on to a watch-glass, rinsing the specimen with a few drops of distilled water, which is rubbed vigorously on the surface to remove as much as possible of any film there may be. In absence of arsenic, etc., the mass detaches easily, leaving the copper clean; but if arsenic is present, it deposits rapidly on the metal and is then extremely difficult to remove; this in itself is a very good preliminary test for arsenic. Stir the liquid in the watch-glass and transfer, by means of a capillary tube, to a wide test tube, rinse in with a little water followed by an amount of (*b*) equal in volume to the aqueous solution already present. Close the mouth of the test tube with a rubber

stopper carrying a short length (about 2·5 inches) of glass tubing, closed at both ends by cotton-wool plugs, and holding between the plugs a strip of reagent paper. Insert a few small lumps of prepared reagent (*d*) into the test tube, replace the rubber stopper and leave for half an hour; if required, add more solid zinc, but without removing the stopper for longer than necessary. The presence of arsenic is indicated by an orange stain at the bottom end of the strip, tailing off into yellow. In absence of arsenic the paper remains white.

Tried on: Samples Nos. 14, 96, 97, 98, 99—Arsenic present; all results positive.
Nos. 1, 35, 13, 33, 19, 90, 69, 22, 82—Arsenic absent and all results negative.

### (X) Cadmium

*Reagents*—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Sodium hydroxide solution (20 per cent.).
(*c*) Potassium cyanide solution (20 per cent.).
(*d*) Dinitrodiphenylcarbazide[8] solution (saturated alcoholic solution).
(*e*) Formalin solution (37 to 41 per cent.).

*Method*—Place 2 drops of (*a*) on the cleaned surface of the specimen and leave to react for 3 minutes. Shake the drop into the well of a white glazed spot-plate, add 2 drops of (*b*), which should render the drops alkaline to litmus, follow with 5 or 6 drops of (*c*), or sufficient only to dissolve the blue cupric hydroxide completely; the majority of any iron or manganese present will remain as light brown and dark brown precipitates respectively. Add 1 drop of (*d*) followed by 4 or 5 drops of (*e*) and stir well until the reddish-brown colour has been dispelled. Cadmium gives a deep green or greenish-blue coloration, developing quickly into a greenish-yellow solution and a blue precipitate. In absence of cadmium, the liquid assumes a greyish-brown colour, slowly developing into a light dirty-brown precipitate and a greyish-brown solution.

Tried on: Samples Nos. 41, 13, 7, 100, 101—Cadmium present; all results positive.
Nos. 40, 35, 54, 21, 22, 11, 1, 43, 37, 16, 19, 15, 45, 38, 60—Cadmium absent and all results negative.

### (XI) Cobalt

*Reagents*—(*a*) Brominated hydrochloric acid (sp.gr. 1·16).
(*b*) Sodium hypophosphite (solid).
(*c*) Ammonium thiocyanate (solid).
(*d*) Ethyl alcohol.
(*e*) *iso*Propyl alcohol.

*Method*—Place 1 drop of (*a*) on the cleaned surface of the specimen, stirring continuously with a pointed glass rod until the drop has become practically white (or fawn). Transfer the drop to a watch-glass, rinse in with 3 or 4 drops of distilled water and add a further drop or two of (*a*) until the liquid is clear. Add approximately 0·1 g. of (*b*), and stir until dissolved, follow with about the same quantity of (*c*) and again stir well. Drop the mixture on to the centre of a filter-disc, supported on the open mouth of a beaker, keeping the solid confined as closely as possible to the centre of the wet patch. Wash four times with 2 or 3-drop quantities of (*d*). Any notable amount of cobalt, *e.g.*, about 2 per cent., is manifested at this stage by the formation of light blue rings passing outwards from the centre; the fourth wash concentrates the cobalt as a band close to the outer edge of the wetted patch. No indication is obtained at this stage from 0·2 per cent. of cobalt. Hang up the paper to dry. The colour with ethyl alcohol is transient and rapidly disappears. When dry, treat the edge of the paper with a few drops of (*e*), then tilt the paper so as to let the liquid run towards the centre of the paper; where the *iso*propyl alcohol cuts the cobalt ring the blue colour is at once reformed. This colour, though transient, is somewhat more permanent than that with ethyl alcohol; it is most vivid as the alcohol dries. The lower limit of 0·2 per cent. is revealed, by careful examination, as a faint blue ring on the outside edge of the paper. In absence of cobalt, or when cobalt is present in quantities less than that stated above, no blue colour is at any stage produced.

Tried on: Samples Nos. 66, 67, 68, 75, 76, 77, 78, 79—Cobalt present; all results positive.
Nos. 1, 17, 22, 15, 48, 52, 54, 42, 55, 14, 13, 16—Cobalt absent and all results negative.

### (XII) Chromium

*Reagents*—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Diluted sulphuric acid (1 + 3).
(*c*) Bromine water.
(*d*) Sodium hydroxide solution (20 per cent.).
(*e*) Diphenylcarbazide solution (1 per cent. in glycerol), 1 vol.; diluted sulphuric acid (1 + 3), 1 vol.

*Method*—Attack the cleaned sample with 2 drops of (*a*) and leave until the attack is complete. Gently remove the liquid by means of capillary tube and add 2 drops of (*b*) to the deposit on the copper surface; after about 1 to 2 minutes, crystals of copper sulphate separate out of solution. Stir the liquid to detach the crystals, etc., and transfer to a clean watch-glass. Add 2 or 3 drops of (*c*), or until present in excess, then follow with 3 or 4 drops of (*d*), which should make the mixture alkaline; if not, more alkali is added until a blue reaction is obtained with litmus paper. Place a 12·5-cm. filter-disc, previously soaked in bromine water and dried, on the open mouth of a beaker and treat the centre with 3 drops of (*e*). Prepare a filter-tube, consisting of a short length of glass tubing, approximately 0·75 × 0·5inch, into the end of which is pressed some filter-paper pulp; place this tube over the wet reagent patch and filter through it the alkaline liquid obtained above, wash once with 3 drops of water, remove the tube and discard it. Add 6 to 8 drops of (*e*) equidistant from the centre of the wet patch and just inside the wet area. Chromium is indicated by an immediate formation of purple crescents at the interface between the alkali chromate and the acid diphenylcarbazide. The coloured pattern of the paper takes the following design: at the centre of the paper is a small colourless area surrounded by a light pinkish band (probably the alkaline reagent colour), which is more pronounced in absence of chromium. Immediately outside the pink band appears the purple colour of chromium, if present; and further out still is the yellow glycerol - reagent colour. The alkaline solution does not spread out uniformly, but tends to break through the periphery at certain points to form a series of inlets. All papers tend to develop a purplish colour after standing for some time, but as little as 0·2 per cent. of chromium should show clearly by the time filtration has ceased. In absence of chromium, the paper appears as described above but without the purple bands just outside the alkaline pink area.

Tried on: Samples Nos. 16, 37, 102, 103, 104, 105—Chromium present; all results positive.
Nos. 43, 41, 4, 14, 11, 25, 45, 19, 49, 6, 21, 60, 22, 40—Chromium absent and all results negative.

### (XIII) Phosphorus

*Reagents*—(*a*) Ammonium persulphate (solid).
(*b*) Diluted ammonia (1 + 3).
(*c*) Potassium cyanide solution (10 per cent.).
(*d*) Diluted nitric acid (sp.gr. 1·20).
(*e*) Ammonium molybdate solution (10 per cent.).
(*f*) Diluted, boiled out, nitric acid solution (5 per cent.).
(*g*) Stannous chloride solution (5 per cent. in 10 per cent. hydrochloric acid).

*Method*—Place a little of the solid (*a*) on the surface of the cleaned specimen and dissolve in 2 drops of (*b*), stir, and leave to stand for 3 to 5 minutes. Add 4 or 5 single drops of (*c*), stir well after each addition; if any blue or green precipitate remains unattacked, a further addition of cyanide should be made; leave for 5 minutes with occasional stirring. Transfer the liquid to a watch-glass, acidify with 2 drops of (*d*), stir, then follow with a small quantity of (*a*), stir again, and leave for a few minutes. As a rule this results in a clear solution, but if there is a precipitate still unattacked, add a little more persulphate and a third drop of (*d*). Regardless of whether there is still any precipitate, the process is proceeded with. One drop of (*e*) is added and thoroughly stirred, and allowed to stand with occasional stirring for at least 10 minutes. Transfer the liquid, slowly in a dropwise manner, to the centre of a filter-paper, to localise the precipitate to a small spot, wash with four 1 or 2-drop quantities of (*f*). When the spreading of the wash-liquor has ceased, add 2 or 3 drops of (*g*), whereupon phosphorus is indicated by a blue spot approximately 1 inch in diameter. High silicon

contents may also result in the formation of a blue spot, but this spot is washed out into a large, faintly blue area by continued treatment with (*g*). Arsenic, if not completely removed by re-deposition on the sample, shows up as a blue ring at the outer edge of the paper upon drying. In absence of phosphorus there is no blue spot at the centre of the paper. The presence of iron, manganese or nickel may result in a brown spot at the centre of the paper, but this should not obscure any reaction due to phosphorus.

Tried on: Samples Nos. 20, 22—Phosphorus present; both results positive.
Nos. 21, 14, 11, 43, 1, 82, 63, 13, 15, 40, 45, 9—Phosphorus absent or less than 0·05 per cent. and all results negative.

## Summary

Tests have been described for the alloying elements in copper-base alloys. The elements so detected are manganese, zinc, tin, iron, lead, silicon, nickel, aluminium, beryllium, arsenic, cadmium, cobalt, chromium and phosphorus.

With the alloys at our disposal all the tests have proved specific and unambiguous, with the exception of silicon which cannot be detected directly in presence of large amounts of cobalt, but the presence of a black insoluble precipitate, when cobalt is known to be present, would indicate silicon.

A new separation of aluminium and beryllium has been described which may provide a useful analytical procedure for the estimation of beryllium in presence of aluminium.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper, and also to Johnson Matthey & Co., Ltd., for the supply of Mallory alloys, 73, 84 and 100.

## Appendix

### Specimens of alloys used in the tests

Constituents, per cent.

| No. | Sample | Mn | Zn | Sn | Fe | Pb | Si | Ni | Al | Be | As | Cd | Co | Cr | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Mn 4 | 28·8 | 1·72 | 0·08 | 0·71 | — | 0·29 | — | — | — | — | — | — | — | — |
| 2 | Mn 3 | 15 | ? | ? | ? | — | ? | — | — | — | — | — | — | — | — |
| 3 | Mn 2 | 6 | ? | ? | ? | — | ? | — | — | — | — | — | — | — | — |
| 4 | RLN | 4·75 | — | — | 0·17 | — | — | — | — | — | — | — | — | — | — |
| 5 | RLQ | 2·3 | — | — | 0·10 | — | — | — | — | — | — | — | — | — | — |
| 6 | TAHU | 2·17 | 31·3 | 0·06 | 1·50 | — | — | — | 4·44 | — | — | — | — | — | — |
| 7 | 880 | — | 0·03 | — | ? | — | — | — | — | — | — | 0·14 | — | — | — |
| 8 | Mn 5 | 1 | ? | ? | ? | — | ? | — | — | — | — | — | — | — | — |
| 9 | MNP | 1·0 | ? | ? | ? | — | ? | — | — | — | — | — | — | — | 0·03 |
| 10 | "7" | 0·4 | 40 | — | 0·2 | — | — | — | — | — | — | — | — | — | — |
| 11 | TAHG | 0·10 | — | — | 5·1 | — | — | 5·2 | 9·6 | — | — | — | — | — | — |
| 12 | Cu/Ni | 0·15 | — | — | — | — | — | 20 | — | — | — | — | — | — | — |
| 13 | RLP | — | — | — | — | — | — | — | — | — | — | 0·45 | — | — | — |
| 14 | RLO | — | — | — | — | — | — | — | — | — | 0·95 | — | — | — | — |
| 15 | SFP | — | — | — | 5·8 | — | — | — | — | — | — | — | — | — | — |
| 16 | SDQ | — | 4·7 | — | — | — | — | — | — | — | — | — | — | 1·15 | — |
| 17 | RLH | — | 30·7 | — | — | — | — | — | — | — | — | — | — | — | — |
| 18 | RBP | — | — | — | — | — | — | — | 5·75 | — | — | — | — | — | — |
| 19 | CuSb | — | — | — | — | — | — | 1·6 | — | — | — | — | — | — | — |
| 20 | P 6 | — | — | — | — | — | — | — | — | — | — | — | — | — | 0·2 |
| 21 | DFL 1 | — | 5·10 | 5·65 | 0·18 | 4·16 | — | 0·12 | — | — | — | — | — | — | — |
| 22 | DRF | — | 2·08 | 9·71 | — | 0·08 | — | — | — | — | — | — | — | — | 0·11 |
| 23 | SEC | — | 17·9 | — | — | — | — | — | — | — | — | — | — | — | — |
| 24 | RLK | — | 14·6 | 2·1 | — | — | — | — | — | — | — | — | — | — | — |
| 25 | SEB | — | 12·5 | — | — | — | — | — | — | — | — | — | — | — | — |
| 26 | SEA | — | 8·81 | — | — | — | — | — | — | — | — | — | — | — | — |
| 27 | SDT | 2·26 | 5·12 | — | 0·10 | — | — | — | — | — | — | — | — | — | — |
| 28 | SDZ | — | 4·82 | — | — | — | — | — | — | — | — | — | — | — | — |
| 29 | S 898 | — | 0·59 | — | — | — | — | — | — | — | — | — | — | — | — |
| 30 | S 897 | — | 0·62 | — | — | — | — | — | — | — | — | — | — | — | — |
| 31 | S 896 | — | 0·19 | — | — | — | — | — | — | — | — | — | — | — | — |
| 32 | L 11 | 0·04 | 0·30 | — | 0·14 | — | — | — | — | — | — | — | — | — | — |
| 33 | IC | 0·01 | 0·26 | — | 0·02 | — | — | — | — | — | — | — | — | — | — |
| 34 | RBS | — | <0·10 | — | — | — | — | 1·0 | 6·0 | — | — | — | — | — | — |
| 35 | RBT | 1·15 | <0·10 | — | 0·34 | — | 2·07 | — | — | — | — | — | — | — | — |
| 36 | RBP | — | <0·10 | — | — | — | — | — | 5·75 | — | — | — | — | — | — |

APPENDIX—*continued*

| No. | Sample | Mn | Zn | Sn | Fe | Pb | Si | Ni | Al | Be | As | Cd | Co | Cr | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 37 | SDP | — | — | — | — | — | — | — | — | — | — | — | — | 0·95 | — |
| 38 | S 876 | — | <0·1 | — | 1·34 | — | — | — | 1·42 | 2·71 | — | — | — | — | — |
| 39 | RBR | — | — | — | — | — | — | 1·0 | 3·90 | — | — | — | — | — | — |
| 40 | Copper | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| 41 | S 883 | — | — | — | — | — | — | — | — | — | — | 2·0 | — | — | — |
| 42 | GM | — | — | — | — | — | — | 20 | — | — | — | — | — | — | — |
| 43 | RRG | — | — | — | — | — | — | 20 | — | — | — | — | — | — | — |
| 44 | Speculum | — | — | 50·0 | — | — | — | — | — | — | — | — | — | — | — |
| 45 | CuSn | — | — | 15·0 | — | — | — | — | — | — | — | — | — | — | — |
| 46 | RLR | — | — | 5·2 | — | — | — | — | — | — | — | — | — | — | — |
| 47 | RLK | — | 14·6 | 2·10 | — | — | — | — | — | — | — | — | — | — | — |
| 48 | RYB | — | 38·7 | 0·50 | 0·10 | 2·05 | — | 0·08 | — | — | — | — | — | — | — |
| 49 | CMC | tr | 40·2 | 0·30 | 0·22 | 1·50 | — | — | — | — | — | — | — | — | — |
| 50 | TNR | — | 40·9 | 0·17 | 0·06 | 0·16 | — | — | — | — | — | — | — | — | — |
| 51 | COB | — | 40 | 0·13 | 0·12 | 1·84 | — | — | — | — | — | — | — | — | — |
| 52 | S 23 | 0·57 | 1·30 | 0·10 | 0·73 | — | 6·84 | — | — | — | — | — | — | — | — |
| 53 | OZN | — | 0·03 | 0·09 | 0·04 | — | — | — | — | — | — | — | — | — | — |
| 54 | SDU | — | — | — | — | — | — | 5·0 | 4·0 | — | — | — | — | — | — |
| 55 | Cu/Be | — | — | — | — | — | — | — | — | 2·34 | — | — | — | — | — |
| 56 | DDU | — | 27 | — | — | — | — | 20 | 0·30 | — | — | — | — | — | — |
| 57 | SDW | — | — | — | — | — | — | 4·85 | 2·0 | — | — | — | — | — | — |
| 58 | SDX | — | — | — | 0·45 | — | — | 4·81 | 0·98 | — | — | — | — | — | — |
| 59 | SDY | — | — | — | 0·21 | — | — | 9·54 | 1·17 | — | — | — | — | — | — |
| 60 | SDR | — | — | — | — | — | 2·4 | — | — | — | — | — | — | — | — |
| 61 | RLM | — | — | — | — | — | 1·25 | — | — | — | — | — | — | — | — |
| 62 | S 15 | ? | ? | ? | ? | — | 1·0 | — | — | — | — | — | — | — | — |
| 63 | S 12 | ? | ? | ? | ? | — | 2·0 | — | — | — | — | — | — | — | — |
| 64 | RLL | — | — | — | — | — | 0·55 | — | — | — | — | — | — | — | — |
| 65 | S 11 | ? | ? | ? | ? | — | 0·50 | — | — | — | — | — | — | — | — |
| 66 | MA 100 | — | — | — | — | — | 0·32 | — | — | 0·42 | — | — | 2·00 | — | — |
| 67 | MA 84 | — | — | — | — | — | 0·34 | — | — | — | — | — | 2·50 | — | — |
| 68 | MA 73 | — | — | — | — | — | 0·07 | — | — | 2·03 | — | — | 0·20 | — | — |
| 69 | RRJ | — | 4·9 | — | — | — | — | 15·6 | — | — | — | — | — | — | — |
| 70 | RRH | — | 9·8 | — | — | — | — | 10·1 | — | — | — | — | — | — | — |
| 71 | SDM | — | 13·9 | — | — | — | — | 9·6 | — | — | — | — | — | — | — |
| 72 | SDO | — | 9·2 | — | — | — | — | 4·9 | — | — | — | — | — | — | — |
| 73 | RBQ | — | — | — | — | — | — | 1·0 | 1·9 | — | — | — | — | — | — |
| 74 | SDN | — | 14·6 | — | — | — | — | 4·6 | — | — | — | — | — | — | — |
| 75 | 922 | — | — | — | — | — | 0·53 | — | — | — | — | — | 2·59 | — | — |
| 76 | 923 | — | — | — | — | — | 3·10 | — | — | — | — | — | 0·65 | — | — |
| 77 | 924 | — | — | — | — | — | 1·23 | — | — | — | — | — | 1·17 | — | — |
| 78 | 925 | — | — | — | — | — | 0·26 | — | — | — | — | — | 0·37 | — | — |
| 79 | 926 | — | — | — | — | — | 3·16 | — | — | — | — | — | 0·77 | — | — |
| 80 | 5 | — | — | — | — | — | — | — | 3·0 | — | — | — | — | — | — |
| 81 | 4 | — | — | — | — | — | — | — | 2·0 | — | — | — | — | — | — |
| 82 | 3 | — | — | — | — | — | — | — | 1·0 | — | — | — | — | — | — |
| 83 | 2 | — | — | — | — | — | — | — | 0·75 | — | — | — | — | — | — |
| 84 | 1 | — | — | — | — | — | — | — | 0·5 | — | — | — | — | — | — |
| 85 | 865 | — | — | — | 1·66 | — | — | — | — | 0·53 | — | — | — | — | — |
| 86 | 866 | — | — | — | 4·13 | — | — | — | — | 0·44 | — | — | — | — | — |
| 87 | 867 | — | — | — | 2·48 | — | — | — | — | 0·98 | — | — | — | — | — |
| 88 | 868 | — | — | — | 1·17 | — | — | — | — | 1·98 | — | — | — | — | — |
| 89 | 869 | — | — | — | 1·68 | — | — | — | — | 0·13 | — | — | — | — | — |
| 90 | 870 | — | — | — | 1·16 | — | — | — | — | 0·43 | — | — | — | — | — |
| 91 | 871 | — | — | — | 1·10 | — | — | — | 0·33 | 1·14 | — | — | — | — | — |
| 92 | 872 | — | — | — | 0·70 | — | — | — | 0·76 | 1·32 | — | — | — | — | — |
| 93 | 873 | — | — | — | 0·31 | — | — | — | 0·46 | 1·44 | — | — | — | — | — |
| 94 | 874 | — | — | — | 1·44 | — | — | — | 1·35 | 1·46 | — | — | — | — | — |
| 95 | 875 | — | — | — | 2·43 | — | — | — | 1·00 | 3·44 | — | — | — | — | — |
| 96 | 884 | — | — | — | 0·38 | — | — | — | — | — | 0·23 | — | — | — | — |
| 97 | 885 | — | — | — | 0·22 | — | — | — | — | — | 0·27 | — | — | — | — |
| 98 | 886 | — | — | — | 0·19 | — | — | — | — | — | 0·51 | — | — | — | — |
| 99 | 887 | — | — | — | 0·49 | — | — | — | — | — | 0·68 | — | — | — | — |
| 100 | 881 | — | 0·07 | — | ? | — | — | — | — | — | — | 0·14 | — | — | — |
| 101 | 882 | — | — | — | ? | — | — | — | — | — | — | 0·50 | — | — | — |
| 102 | RLD | — | — | — | — | — | — | — | — | — | — | — | — | 0·22 | — |
| 103 | RLE | — | — | — | — | — | — | — | — | — | — | — | — | 0·35 | — |
| 104 | RLF | — | — | — | — | — | — | — | — | — | — | — | — | 0·12 | — |
| 105 | RLG | — | — | — | — | — | — | — | — | — | — | — | — | 0·22 | — |

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# The Micro-Estimation of Cadmium

BY F. P. DWYER AND N. A. GIBSON

SYNOPSIS—A new reagent, triphenylmethylarsonium iodide, is recommended for the nephelometric and gravimetric estimation of cadmium in the presence of zinc. The nephelometric procedure is suitable in the range 1 to 100 μg. of cadmium per ml., with an accuracy of approximately 5 per cent., and the gravimetric procedure for the estimation of quantities of the order of 10 mg., with an accuracy of 1 per cent. The accuracy of the nephelometric method, however, decreases markedly when the comparative standard and the unknown solution are far apart in concentration.

THE usual method for the quantitative estimation of cadmium depends upon the formation of sparingly soluble salts of the type $R_2CdX_4$ (X = I or CNS), in which an organic base of high molecular weight is used as the cation. Many reagents based on this principle, however, fail to separate cadmium from zinc, whilst others are unsatisfactory because of the tendency of excess of reagent to be occluded, lack of definite composition, or unsuitable physical properties of the precipitate. The most valuable reagent appears to be trimethylphenyl ammonium iodide,[1] but the solubility of the salt $(Me_3PhN)_2CdI_4$ limits its applicability for much less than 1 mg. of the metal. The colorimetric method using dithizone, developed by Fischer and Leopoldi,[2] is claimed to be suitable in the range 1 to 100 μg. of cadmium, but as this reagent forms coloured complexes with many metals, considerable care must be exercised in its use. Micro-quantities of the metal can be estimated by spectrographic and polarographic methods, and it is claimed by Hammond[3] that these are the only completely satisfactory procedures, since a specific quantitative reagent for cadmium has not yet been found.

The quaternary arsonium salts of the tetraiodocadmate ion $(CdI_4)''$ have been described in a previous paper,[4] in which it was shown that with several of the arsonium iodides, cadmium could be detected at concentrations below 1 μg. per ml. The salts $(R_4As)_2CdI_4$ had very high molecular weights, and separated usually as almost colloidal suspensions, which appeared to be suitable for the nephelometric estimation of cadmium in the presence of zinc. This observation has now been confirmed, and the reagent triphenylmethylarsonium iodide is put forward as suitable for the nephelometric estimation of cadmium in the concentration range of 1 to 100 μg. per ml., and for the gravimetric estimation of 1 to 100 mg.

## THE NEPHELOMETRIC ESTIMATION OF CADMIUM

REAGENTS AND APPARATUS—Pure recrystallised triphenylmethylarsonium iodide[4] was dissolved in 0·5 per cent. potassium iodide solution so as to obtain a 0·5 per cent. solution. This solution was almost saturated with respect to the arsonium salt. The protective colloid solution, a 1 per cent. solution of gelatin, was prepared freshly each week. The standard cadmium salt solution (1000 μg. of cadmium per ml.) was prepared by dissolving A.R. cadmium oxide in a slight excess of dilute sulphuric acid, and diluted as required. The opacity of the solutions was determined with a Spekker photo-absorptiometer, with neutral filters H508. The cells were 10 mm. thick (capacity, 9 ml.) for solutions containing from 1 to 10 μg. of cadmium per ml., and 2·5 mm. thick (capacity, 2 ml.) for solutions containing from 10 to 100 μg. of cadmium per ml.

PROCEDURE—(*a*) *Solutions containing* 1 *to* 8 *μg. of cadmium per ml.*—Reference solution: 10 μg./ml. The test and the reference solutions (10 ml.) in separate test tubes were each treated with gelatin solution (2 drops) and mixed thoroughly. To both, simultaneously, the reagent solution (5 ml.) was then added, and after stirring, each was transferred at once to the absorptiometer tubes.

(*b*) *Solutions containing* 10 *to* 100 *μg. of cadmium per ml.*—Reference solution: 100 μg./ml. In this concentration range, 2 ml. each of the reference and test solutions were used, with 2 drops of gelatin solution as before, and 1 ml. of the reagent.

The reference solution increased in optical density for 10 to 15 minutes after the addition of the reagent, remained steady at this maximum for a further 10 to 15 minutes, after which the white precipitate of the complex salt began to separate. It was usually an hour before the separation was visible. The reading for the test solution was the mean of the readings taken while the reference solution gave a steady reading, one reading being taken each minute for 6 minutes. A greater volume of the gelatin solution unnecessarily prolonged the time required for the estimation, without improving the reproducibility of the readings. The effect of raising the temperature was to decrease the time required to reach the maximum optical density, which was itself reduced, but in the range 15° to 25° C. these effects were not significant. The acidity of the solutions was not critical, and usually lay between 0·01 and 0·001 *N*.

Calibration curves were constructed for each range of concentrations, using the mean value of six determinations for each point on the curve. The results obtained by the use of these curves are shown in Tables I and II.

TABLE I

SAMPLES CONTAINING 1 TO 8 μG. OF CADMIUM PER ML. COMPARED WITH REFERENCE SOLUTION CONTAINING 10 μG./ML.

| Cd used, μg./ml. | Found | | Mean deviation, μg./ml. | Mean deviation, % |
|---|---|---|---|---|
| | Max. | Min. | | |
| 1 | 1·25 | 0·85 | 0·15 | 15 |
| 2 | 2·40 | 1·55 | 0·35 | 18 |
| 4 | 4·35 | 3·60 | 0·35 | 9 |
| 6 | 6·70 | 5·55 | 0·40 | 7 |
| 8 | 8·35 | 7·80 | 0·20 | 3 |

TABLE II

SAMPLES CONTAINING 10 TO 80 μG. OF CADMIUM PER ML. COMPARED WITH REFERENCE SOLUTION CONTAINING 100 μG./ML.

| Cd used, μg./ml. | Found | | Mean deviation, μg./ml. | Mean deviation, % |
|---|---|---|---|---|
| | Max. | Min. | | |
| 10 | 12·0 | 7·5 | 1·0 | 10 |
| 20 | 21·0 | 18·5 | 1·0 | 5 |
| 40 | 41·5 | 39·0 | 0·5 | 1·3 |
| 60 | 62·5 | 58·5 | 1·0 | 1·7 |
| 80 | 81·5 | 78·5 | 1·0 | 1·3 |

TABLE III

CADMIUM IN PRESENCE OF A HUNDREDFOLD QUANTITY OF ZINC

Reference solution: 10 μg./ml. or 100 μg./ml. as appropriate

| Cd used, μg./ml. | Mean Cd found (without additional KI) | Mean deviation, % | Mean Cd found (with additional KI) | Mean deviation, % |
|---|---|---|---|---|
| 1·0 | 1·2 | 20 | 1·35 | 35 |
| 8·0 | 6·9 | 14 | 7·9 | 1·3 |
| 10·0 | 7·0 | 30 | 11·3 | 13 |
| 80·0 | 72·5 | 9 | 81·2 | 1·5 |

In order to test the suitability of the reagent in presence of large amounts of zinc, solutions were prepared containing 100 times as much of this metal as cadmium. Employing the procedures above, only part of the complex cadmium salt was obtained, owing to the reduction in iodide ion concentration by the formation of the $ZnI_4''$ ion. This difficulty was overcome by addition of 1 or 2 drops of 10 per cent. potassium iodide solution. The results of a series of tests are shown in Table III.

### The micro-gravimetric estimation of cadmium

A solution of cadmium sulphate (50 ml.), containing 10 mg. of cadmium, was heated to boiling-point, and the triphenylmethylarsonium iodide reagent (50 ml., three equivalents), was added slowly, with stirring. The mixture was allowed to stand for 1 hour to cool, and then cooled in running water for a further half-hour. The precipitate was collected in a sintered-glass filter (porosity 4), washed with 0·5 per cent. potassium iodide solution, and dried at 105° to 110° C. The compound $(Ph_3MeAs)_2CdI_4$ contains 8·903 per cent. of cadmium. The results of typical determinations are shown in Table IV.

Table IV

| Cd used, mg. | Cd found, mg. | Percentage error |
|---|---|---|
| 10 | 9·94 | − 0·6 |
| 10 | 9·99 | − 0·1 |
| 10 | 10·04 | + 0·4 |
| 10 | 10·05 | + 0·5 |
| 11* | 11·06 | + 0·5 |
| 11* | 11·19 | + 1·7 |
| 12* | 11·78 | − 1·8 |
| 12* | 12·19 | + 1·6 |

* Determinations made by students.

In the presence of zinc acetate (3·36 g., equivalent to 1 g. of zinc, or 100 times the amount of cadmium) it was necessary to add 10 ml. of 10 per cent. potassium iodide solution in order to precipitate the cadmium quantitatively, but as shown in Table V, the reagent is equally satisfactory in such large concentrations of zinc.

Table V

| Cd used, mg. | Cd found, mg. | Percentage error |
|---|---|---|
| 10·00 | 10·06 | 0·6 |
| 10·00 | 10·06 | 0·6 |
| 10·00 | 10·09 | 0·9 |

In both the nephelometric and gravimetric methods using this reagent, interference is caused by silver, lead, mercury, copper, bismuth, antimony and arsenic, which either form insoluble iodides or similar complex compounds. As has already been shown by Pass and Ward,[1] these elements are easily eliminated by boiling the acid solution with iron wire and filtering before addition of the reagent.

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*July*, 1949

# The Spectrophotometric Determination of Small Amounts of Hydrogen Peroxide in Aqueous Solutions*

By T. C. J. OVENSTON and W. T. REES

Synopsis—An accurate and precise method for the determination of microgram quantities of hydrogen peroxide in neutral aqueous solutions is described. The method depends on the liberation of iodine by the action of the hydrogen peroxide on potassium iodide, the reaction being catalysed by ammonium molybdate. The iodine liberated is determined by measurement of the absorption by the periodide ion at a wavelength of 353 mμ.

The comparative merits of the periodide and the starch-iodine methods for the absorptiometric determination of liberated iodine are examined, and comparison is made with the peroxidised titanium method for the determination of hydrogen peroxide.

When hydrogen peroxide is added to a solution containing an excess of iodide, iodine is set free according to the reaction

$$H_2O_2 + 2I' \rightarrow 2OH' + I_2.$$

The use of this reaction for the determination of hydrogen peroxide was proposed by Planes.[1] The reaction is slow in neutral solution but the rate increases with fall of pH, although the presence of acid accelerates the photolysis of the unused iodide and leads to erratic results.

Of the other absorptiometric methods which have been proposed, probably the most satisfactory is that based on the formation of the yellow complex when hydrogen peroxide is added to titanium sulphate in acid solution. This method has been adapted for abridged spectrophotometry by Allsopp[2] and by Eisenberg.[3]

Preliminary experiments suggested that the iodine method was very much more sensitive than the titanium method, and the iodine method was chosen for the present investigation when it was found that the reaction in neutral solution could be accelerated sufficiently by the addition of a small amount of ammonium molybdate. This catalyst has been employed in a titrimetric procedure using the same reaction.[4]

The purpose of this paper is to assess the merits of the principal methods available for the measurement of the liberated iodine, and to present a rapid and accurate method for determining microgram quantities of hydrogen peroxide in aqueous solutions.

In earlier work, the liberated iodine has been commonly determined by adding starch solution and comparing the blue colour of the starch - iodine complex with that of standards. This method has been studied very fully and it has been shown to possess some serious drawbacks. Starch itself is a material of variable composition, its two principal constituents being amylose and amylopectin. Amylose gives with iodine (in the presence of iodide) a deep blue complex, and amylopectin gives a somewhat less intense violet colour. The colour obtained with different batches of starch is thus liable to vary. In addition, the colour intensity is dependent on the concentration of iodide and the temperature of the solution, and it also lacks stability. Nevertheless, a fair degree of precision is possible if conditions are carefully controlled.

* After this paper had been written, another paper describing a spectrophotometric method for the determination of small concentrations of hydrogen peroxide was noted (Patrick, W. A., and Wagner, H. B., *Anal. Chem.*, 1949, **21**, 1279). The method is similar in principle to that described in the present paper, except that the liberation of iodine is carried out in an acid medium similar to that used in experiment D under the heading "Effect of acidity." The present writers are of the opinion that the optimum conditions for accurate quantitative work are obtained only when using an approximately neutral medium. In further confirmation of this, ten tests were made by each method, using 8·6 μg. of hydrogen peroxide in each test. The results can be summarised in the following way—

| | Blank reading | | Test reading | | Test corrected for blank | |
|---|---|---|---|---|---|---|
| Method | Mean E | Standard deviation | Mean E | Standard deviation | Mean E | Standard deviation |
| Ovenston and Rees | 0·0077 | 0·00067 | 0·7010 | 0·00245 | 0·6933 | 0·00275 |
| Patrick and Wagner | 0·0282 | 0·00567 | 0·7354 | 0·00977 | 0·7072 | 0·01268 |

The adherents of the starch - iodine technique have possibly been influenced by the apparently high sensitivity of the method when the colour is examined visually. Even when using a photo-electric absorptiometer, Sendroy[5] concluded that the relative colour intensity of the starch - iodine complex was about a hundred times that of the yellow colour of the periodide ($I_3'$) ion present in iodine - iodide solutions, which also is proportional to the iodine content. However, Sendroy had employed filter systems which were decidely favourable to the starch - iodine method. Despite this, he recognised that the measurement of the yellow periodide was more convenient and gave more accurate results, and later, with Alving,[6] he found that the sensitivity could be increased at least fiftyfold by means of filters transmitting more in the ultra-violet.

Further spectrophotometric studies of the starch - iodine method have been made by Bairstow[7] and Pieters and Hanssen,[8] who have recommended it for the determination of the iodine liberated (in an adaptation of the Winkler method for oxygen in water), provided that suitable precautions are taken to ensure temperature control and standardisation of starch supply. Gross[9] has recommended spectrophotometric measurement of the absorption by the blue complex at a wavelength of 575 m$\mu$.

Another method of measuring the liberated iodine depends on extraction with a solvent such as carbon disulphide, carbon tetrachloride or chloroform to give a violet solution. The efficiency of extraction of iodine from the aqueous phase depends very much on the concentration and nature of the salts present, and methods relying on a single partition therefore tend to be unreliable. At the same time, if the iodine is removed completely by a series of extractions, the total volume of the solvent so accumulated is so large that the sensitivity of the test is seriously reduced, concentration being impracticable owing to the volatility of the iodine.

Very recently, spectrophotometric methods for the determination of liberated iodine by means of the periodide ion have been reported by Shahrokh and Chesbro[10] and by Custer and Natelson,[11] extinction measurements being made in each case with a Beckman quartz spectrophotometer. The latter authors published absorption spectra of iodine in water, potassium iodide solutions, benzene, toluene, alcohol and chloroform, but did not study the starch - iodine complex. Of these spectra, that for iodine in potassium iodide showed the strongest absorption bands.

## Comparison of sensitivities of methods for photo-electric spectrophotometry

Measurements were made with a Beckman quartz spectrophotometer (model DUV), using the tungsten-filament source at wavelengths above 320 m$\mu$. and the hydrogen-arc source at lower wavelengths. Absorption spectra of six solutions were plotted, the concentration of free iodine being 4·5 $\mu$g. per ml. throughout. The solutions were—

A. 0·0002 *M* potassium iodide solution containing 500 $\mu$g. of starch per ml.
B. 0·002 " " " " " " "
C. 0·01 " " " " " " "
D. 0·1 " " " " " " "
E. 0·1 *M* potassium iodide, without starch.
F. Pure chloroform.

The starch was typical material supplied by the British Drug Houses Ltd. The starch - iodine colours were all developed and measured at 20° C., and the spectra are shown in Fig. 1. The absorption due to the chloroform solution is so small in relation to the other solutions as to require no further consideration in the present work.

For this concentration of iodine, at 20° C., it appears that the most intense absorption by the starch - iodine complex occurs in about 0·01 *M* potassium iodide solution. There is an indication of the formation of a different complex at higher concentrations of potassium iodide. The largest specific extinction for the starch - iodine system at 20° C., as obtained from curve C (Fig. 1) at 605 m$\mu$., is 0·147 per cm. per p.p.m. of iodine. The corresponding values for the periodide ion in 0·1 *M* potassium iodide, as obtained from curve E (after correction for the absorption due to the presence of iodide), are 0·107 per cm. per p.p.m. of iodine at 353 m$\mu$. and 0·145 per cm. per p.p.m. of iodine at 289 m$\mu$. Using photo-electric receivers of adequate sensitivity for the various wavelengths concerned, the sensitivity of the periodide method is much greater than has generally been supposed, and is, in fact, about as sensitive as the starch - iodine method if measurements are made at 289 m$\mu$. Even if measurements are made at 353 m$\mu$., the periodide method still possesses three-quarters of the sensitivity of the starch - iodide method. In view of the many factors which render

the starch - iodide method liable to error, the best method for photo-electric measurement is clearly that using the absorption in the near ultra-violet part of the spectrum by the periodide ion.

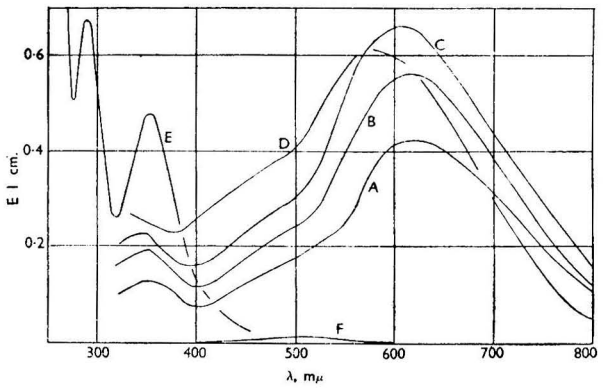


Fig. 1. Absorption spectra, based on an iodine concentration of 4·5 μg. per ml. Curves A, B, C, and D, starch - iodine complex developed with 0·0002 *M*, 0·002 *M*, 0·01 *M* and 0·1 *M* potassium iodide respectively. Curve E, $I_3'$ complex developed with 0·1 *M* potassium iodide. Curve F, iodine in pure chloroform.

CHOICE OF WAVELENGTH—

Extinction - concentration graphs (not reproduced here) were plotted for various iodine concentrations in 0·1 *M* potassium iodide. In each case Beer's law was obeyed, but the error for measurements made at 289 mμ. was about four times as great as for those made at 353 mμ. There seems nothing to be gained by using the more intense peak, therefore, and all subsequent measurements of the periodide absorption were made at 353 mμ.

EFFECT OF POTASSIUM IODIDE CONCENTRATION—

The effect of potassium iodide concentration on the specific extinction at 353 mμ. was briefly examined. Fig. 2 shows the relation between the concentration of the potassium iodide and extinction for an iodine concentration at 6·3 μg. per ml. The slope of the curve is very slight for 0·1 *M* potassium iodide, and this strength was used for the determination of hydrogen peroxide.

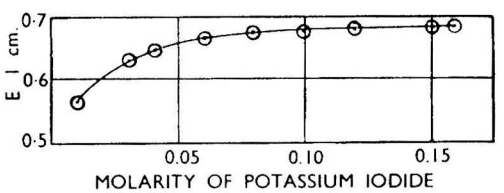


Fig. 2. Effect of concentration of potassium iodide on the development of the $I_3'$ complex (extinction measurements at 353 mμ).

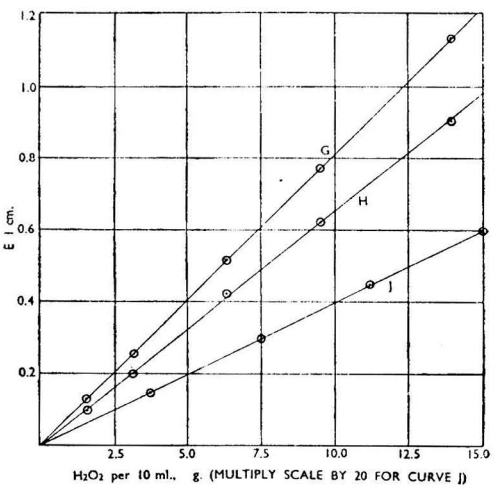


Fig. 3. Standard curves. Curve G, $I_3'$ method at 353 mμ. Curve H, $I_3'$ method adapted for Spekker absorptiometer. Curve J, Titanium method at 410 mμ.

## Recommended method

Reagents—

*Potassium iodide*—0·2 *M* solution. If stored in the dark this will last at least a week. An increase in the extinction of the reagent blank indicates that it requires renewal; this value was normally about 0·010 in the present investigation.

*Ammonium molybdate*—0·5 per cent. w/v solution.

*Hydrogen peroxide*—0·0003 per cent. w/v solution. This is used for preparation of the calibration graph, and may be prepared by volumetric dilution of 0·03 per cent. w/v hydrogen peroxide which has been standardised against permanganate after thousandfold dilution of purest 30 per cent. reagent.

Procedure—

Take a volume of the neutral sample solution not exceeding 4 ml., containing not more than about 12 μg. of hydrogen peroxide, in a 10-ml. calibrated flask. Add 5 ml. of 0·2 *M* potassium iodide solution and 0·1 ml. of 0·5 per cent. w/v ammonium molybdate solution and dilute to the mark at 20° C. Allow to stand in the dark for 5 minutes and then measure the extinction of the solution at 353 mμ. using a 1-cm. cell. Correct this reading for actual cell thickness and subtract the extinction reading of the reagent blank, prepared similarly and at the same time, but with 4 ml. of water in place of the sample. Derive the hydrogen peroxide content of the sample by reference to a calibration graph prepared in the usual way by taking known amounts of 0·0003 per cent. w/v hydrogen peroxide covering the desired range, and plotting the weight against the extinction measurements after correction for the extinction of the reagent blank.

## Adaptation of method for use with a Spekker photo-electric absorptiometer

Although the best results are obtained with a prism spectrophotometer, it is possible to use a photo-electric filter absorptiometer with very little loss of sensitivity. Using a mercury-arc lamp as source, a suitable filter combination consists of Calorex heat absorbing filters together with Wood's glass filters to isolate the 365-mμ. mercury line.

## Effect of acidity

In order to demonstrate the advantage of using an approximately neutral medium for the liberation of the iodine, a series of five experiments, A, B, C, D and E (Table I), were conducted in which various amounts of sulphuric acid were added, the determinations being otherwise as described in the recommended method. The same amount of hydrogen peroxide, 8·9 μg., was present in each test, and a blank was run in the absence of peroxide in every experiment. The acid included in each experiment was sufficient to render the normality of the final 10 ml. of solution equal to the following values—

| Experiment | A | B | C | D | E |
|---|---|---|---|---|---|
| Final normality of $H_2SO_4$ .. | nil* | 0·01 | 0·1 | 0·2 | 1·0 |

* No acid added.

Extinction readings at 353 mμ. were taken over a period of time, the solutions being kept in the dark, and the results obtained are given in Table I.

It is clear from these experiments that the rate of further liberation of iodine from the potassium iodide increases markedly with increase of acidity, and that even a small amount of acid causes a comparatively large increase in the magnitude of the "blank" reading. In experiment A (no acid) a decrease instead of an increase in the extinction reading of the test solution was eventually recorded. This decrease became noticeable after the solution had stood for half an hour, and is typical of other similar experiments carried out by the recommended method.

## Discussion

This method has been developed mainly for the determination of very small concentrations of hydrogen peroxide in pure water and in neutral salt solutions. The presence of large amounts of fluoride, chloride and bromide ions were shown to have no measurable influence on the absorption of the periodide solution.

The degree of accuracy that may be expected is shown by the position of the points from which the calibration graph was obtained; this graph is reproduced in Fig. 3 as curve

G. Curve H in the same figure is the corresponding graph obtained using a Spekker photoelectric absorptiometer with a mercury-arc source and the filters already mentioned. With monochromatic radiation of 353 mμ., unit extinction per cm. is obtained with 12·4 μg. of hydrogen peroxide per 10 ml. of final solution. The corresponding figure with the recommended filter system is 15·4 μg.

As a matter of interest, and as it might possibly be of use at higher concentrations of hydrogen peroxide, the titanium method was given a trial. The conditions specified by Allsopp[2] were followed, except that monochromatic radiation at 410 mμ. (the absorption maximum of the peroxidised titanium system) was used. The calibration graph is shown as curve J in Fig. 3, and the accuracy is again very good. However, it is well known that

TABLE I

EXTINCTION READINGS AT 353 Mμ.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Experiment A | Time, min. | .. | 5 | 10 | 15 | 32 | 60 | 90 | 115 |
| | $E_{1\,cm.}$ | Test* .. | 0·725 | 0·725 | 0·721 | 0·725 | 0·717 | 0·695 | 0·685 |
| | | Blank .. | 0·010 | 0·010 | 0·010 | 0·010 | 0·010 | 0·010 | 0·010 |
| Experiment B | Time, min. | .. | 3 | 5 | 18 | 48 | 130 | | |
| | $E_{1\,cm.}$ | Test* .. | 0·720 | 0·720 | 0·730 | 0·740 | 0·750 | | |
| | | Blank .. | 0·030 | 0·028 | 0·035 | 0·050 | 0·063 | | |
| Experiment C | Time, min. | .. | 3 | 5 | 12 | 32 | 70 | 140 | |
| | $E_{1\,cm.}$ | Test* .. | 0·738 | 0·748 | 0·750 | 0·765 | 0·789 | 0·858 | |
| | | Blank .. | 0·036 | 0·037 | 0·040 | 0·050 | 0·070 | 0·105 | |
| Experiment D | Time, min. | .. | 4 | 5 | 19 | 49 | 69 | 119 | |
| | $E_{1\,cm.}$ | Test* .. | 0·750 | 0·750 | 0·780 | 0·828 | 0·859 | 0·898 | |
| | | Blank .. | 0·050 | 0·050 | 0·063 | 0·081 | 0·089 | 0·145 | |
| Experiment E | Time, min. | .. | 3 | 6 | 18 | 48 | 73 | | |
| | $E_{1\,cm.}$ | Test* .. | 0·778 | 0·802 | 0·866 | 0·933 | 1·040 | | |
| | | Blank .. | 0·103 | 0·109 | 0·130 | 0·198 | 0·236 | | |

* The values of E recorded for the tests have not been corrected for their corresponding blanks.

many anions, particularly fluorides, have a profound effect on the formation of the peroxidised titanium complex, and the authors consider it safer to use the more sensitive periodide method wherever practicable. The range of the periodide method may be extended by volumetric dilution of the sample. Conversely, its sensitivity may be increased to a limited extent by the use of cells of greater optical depth, provided that their working capacity does not exceed 10 ml.

This paper is published with the approval of the Lords Commissioners of the Admiralty, but the responsibility for any statements of fact or opinions expressed rests solely with the authors.

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ADMIRALTY MATERIALS LABORATORY
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*January*, 1950

# The Colorimetric Determination of Small Amounts of Hydrogen Sulphide in Effluent Gases by Means of the Spekker Absorptiometer

By C. G. ETHRINGTON, D. WARREN and F. C. MARSDEN

Synopsis—The determination of small amounts of hydrogen sulphide in effluent gases can be carried out in the presence of excess sulphur dioxide and carbon disulphide, using a method based on the formation of an arsenious sulphide sol in the presence of a protective colloid. Interference from sulphur dioxide is avoided by maintaining the pH at 5·0.

In the course of an investigation on the reaction between hydrogen sulphide and sulphur dioxide in effluent gases, it was necessary to carry out a large number of determinations of hydrogen sulphide in the mixed gases. A number of methods for the determination of hydrogen sulphide in air have been devised,[1,2,3,4,5,6] but were regarded as unsuitable for one reason or another. For example, the commonly used lead acetate paper method[1] was not suitable because (*a*) it was not sufficiently accurate, as it was designed to give a rapid indication of the relative safety of the atmosphere, and (*b*) it was demonstrated that the papers were affected by the sulphur dioxide present, the stains produced being less intense.

Cadmium salts are widely used for the determination of small amounts of hydrogen sulphide,[4] but in the presence of sulphur dioxide the method is not quantitative, and there is also the possibility of formation of cadmium sulphite, which interferes. Again, cadmium sulphide is sparingly soluble in sulphurous acid, and this may lead to low results.

A colorimetric method[4] has been suggested in which the hydrogen sulphide is absorbed in 6 per cent. solution of sodium hydroxide, but this method could not be used because of the presence in the gases of carbon disulphide, which forms thiocarbonates with the sodium hydroxide, and these in turn break down to give sodium sulphide.

It is a well known fact that hydrogen sulphide and sulphur dioxide do not react in alkaline solution, and it was suggested that a weakly alkaline solution of ammonium arsenite should be used as the absorbing medium. Ammonium arsenite was chosen because the thioarsenious acid, which is formed when the pH of the solution is lowered, breaks down to give arsenious sulphide and hydrogen sulphide.

$$2H_3AsS_3 = As_2S_3 + 3H_2S$$

If the pH of the solution is kept above 4·5 there is no interference from sulphite, but trouble was experienced in the first instance due to flocculation of arsenious sulphide; this however was avoided by the addition of the protective colloid, gelatin. It was found that by absorbing the mixed gases in ammonium arsenite solution at a pH between 8·0 and 8·5, and then reducing the pH to 5·0 in the presence of gelatin, the yellow arsenious sulphide sol which was produced could be used as a basis for the colorimetric determination of hydrogen sulphide. When the pH was reduced below 4·0, an opalescence caused by precipitated sulphur interfered with the determination.

## Method

Solutions—

All reagents should be A.R. quality.

*Ammonium arsenite*—Dissolve approximately 1·0 g. of arsenious oxide in the minimum amount of ammonium hydroxide (sp.gr. 0·880), and then remove the excess ammonia by adding *N* hydrochloric acid, using phenolphthalein as indicator; make up to 1 litre.

*Sodium acetate - acetic acid*—Buffer solution.[7] Take 95 ml. of 0·2 *N* acetic acid and mix with 5 ml. of 0·2 *N* sodium acetate. The buffer should be checked by means of the pH meter before use.

*Gelatin*—Dissolve pure gelatin in distilled water to make a 1 per cent. solution. This solution must be freshly prepared.

PROCEDURE—

Place 5 ml. of ammonium arsenite solution and 10 ml. of water in a suitable absorption tube, and aspirate a known volume of the mixed gases through the solution at the rate of 500 ml. per minute. When aspiration is complete, transfer the contents of the tube quantitatively to a 50-ml. graduated flask; add 5 ml. of gelatin solution, and enough acetate buffer to reduce the pH to 5·0. Care must be taken when adding the buffer to avoid local reduction of pH below this value, as it may cause the development of an opalescence. The solution is made up to the 50-ml. mark and allowed to stand for 15 minutes before matching. Prepare a blank by aspirating a similar volume of gas through an absorption tube containing the reagent, but do not develop the arsenious sulphide sol; use this in the subsequent determination on the Spekker.

SPEKKER GRAPH—

A series of standards is prepared by taking aliquots of a standard solution of sodium sulphide which should be checked immediately before and after use. The standards are prepared by taking known amounts of the sodium sulphide solution in increments of 100 $\mu$g., a suitable range being from 0 to 800 $\mu$g.; the standards are then treated as above and, after 15 minutes, the absorption is measured on the Spekker absorptiometer, using Ilford blue filters No. 602, with a zero setting and 4-cm. cells. Alternatively, Hilger O.B.1 filters, which approximately double the sensitivity, can be used. A typical series of standards is as follows—

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $H_2S$ added, $\mu$g. .. | 78 | 156 | 234 | 312 | 390 | 450 | 630 | 672 |
| Drum reading .. | 0·018 | 0·033 | 0·049 | 0·064 | 0·080 | 0·093 | 0·140 | 0·152 |

DISCUSSION—

Spekker graphs were prepared from hydrogen sulphide water and sodium sulphide solution in the presence of 6000 $\mu$g. of sulphur dioxide and 2000 $\mu$g. of carbon disulphide, but no interference was observed so long as the pH was kept above 5·0; below 4·5 an opalescence developed which caused serious interference.

It will be seen that the graph deviates from linearity when the solution contains more than 600 $\mu$g. of hydrogen sulphide, and the effective working range is 100 to 600 $\mu$g. of hydrogen sulphide.

During the absorption of the gases, a second tube containing ammonium arsenite solution was placed in series, but no colour developed when the buffer solution was added. The volume of mixed gases aspirated through the ammonium arsenite should be such that about 400 $\mu$g. of hydrogen sulphide are present in the solution, this volume being determined empirically.

Finally, series of solutions were prepared in which the hydrogen sulphide contents were unknown to the analyst, and the concentrations were determined by the above method. The results were reproducible and the error did not, with one exception in series 3, exceed 5 per cent. over the range 100 to 600 $\mu$g.

SERIES 1

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2S$ added, $\mu$g. .. | 45 | 90 | 156 | 270 | 305 | 312 | 320 | 360 | 390 | 426 | 450 | 474 | 512 | 512 |
| $H_2S$ found, $\mu$g. .. | 48 | 88 | 158 | 260 | 304 | 306 | 325 | 358 | 381 | 410 | 442 | 478 | 500 | 520 |

SERIES 2

Containing 6000 $\mu$g. of $SO_2$

| | | | | | |
|---|---|---|---|---|---|
| $H_2S$ added, $\mu$g. .. | 84 | 210 | 336 | 462 | 588 |
| $H_2S$ found, $\mu$g. .. | 100 | 208 | 344 | 470 | 588 |

SERIES 3

Containing 6000 $\mu$g. of $SO_2$ and 2000 $\mu$g. of $CS_2$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2S$ added, $\mu$g. .. | 63 | 274 | 405 | 411 | 544 | 548 | 685 |
| $H_2S$ found, $\mu$g. .. | 72 | 234 | 420 | 414 | 546 | 556 | 700 |

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COURTAULDS LTD.
RED SCAR WORKS
PRESTON

*June*, 1949

# A Colorimetric Method for the Micro-Determination of Calcium in Plant Tissue Extracts

BY A. J. McGREGOR

SYNOPSIS—Calcium is extracted from fresh or dried plant material by an acetate reagent and precipitated as oxalate. The washed and centrifuged precipitate is used to reduce the red colour of a standard ferric thiocyanate solution. The decrease in intensity of colour, measured absorptiometrically, is proportional to the calcium content of the extract. Magnesium does not interfere.

At very low concentrations the accuracy is of the order of 8 per cent., but over the range 24 to 60 parts of calcium per million the accuracy of repetition is within 2 per cent. Over a similar range of calcium concentrations the results are in close agreement with those obtained by permanganate titration. Added calcium is recovered to within about 2 per cent.

WHAT is known as "lime deficiency" in soils is a common cause of partial failures of crops. The calcium status of the soil is reflected in that of the crop. A deficiency of calcium not great enough to produce visible signs of crop failure may injure quality, *e.g.*, in peas, or lead to risk of calcium deficiency in animals consuming fodder crops. A prompt diagnosis of unsatisfactory nutrient levels in a crop may be important and can be most effectively ascertained by tests performed on the growing plants. The method described below is designed to determine colorimetrically the calcium extractable by a reagent solution from fresh or dried plant material. As the method is rapid and simple it may be found useful for control in vegetable-processing factories as well as for agricultural advisory purposes.

Essentially the method consists of precipitating the calcium as calcium oxalate, washing and centrifuging the precipitate and determining the amount of calcium by the reduction in colour of a standard ferric thiocyanate solution. The intensity of colour developed is measured in a Spekker absorptiometer. The method has proved satisfactory as a routine procedure and gives results that are ordinarily accurate to 2 per cent.

The ability of oxalates to reduce ferric thiocyanate was utilised by Marriott and Howland[1] in a method for the determination of calcium in blood. The method here described is a modification of this procedure and is applicable to plant extracts. The ferric thiocyanate reagent used is capable of estimating 0·05 to 0·6 mg. of calcium in 10 ml.

## METHOD

### REAGENTS

(1) *Acetate reagent*—30 ml. of glacial acetic acid (A.R.) are dissolved in 1 litre of a solution containing 100 g. of hydrated sodium acetate (A.R.).

(2) *Oxalate reagent*—4 g. of ammonium oxalate (A.R.) are dissolved in 100 ml. of distilled water.

(3) *Wash solution*—Prepared by mixing together 2 ml. of concentrated ammonia solution (sp.gr. 0·88), 98 ml. of distilled water, 100 ml. of redistilled ether and 100 ml. of redistilled ethyl alcohol.

(4) *Diluted hydrochloric acid*—50 ml. of concentrated hydrochloric acid (A.R.) are dissolved in distilled water and made up to 1 litre.

(5) *Ferric chloride solution*—8 g. of hydrated ferric chloride (A.R.) are dissolved in 500 ml. of reagent (4), made up to 1 litre with that reagent and filtered through No. 42 Whatman filter-paper.

(6) *Potassium thiocyanate*—16 g. of potassium thiocyanate (A.R.) are dissolved in distilled water and made up to 1 litre.

(7) *Thiocyanate reagent*—10 ml. of ferric chloride reagent (5) and 10 ml. of potassium thiocyanate reagent (6) are measured into a 200-ml. volumetric flask and made up to volume with distilled water. The reagent is allowed to stand for half an hour before use.

(8) *Standard calcium solution*—1·4984 g. of calcium carbonate (A.R.) (oven-dried) are dissolved in acetate reagent (1) and made up to 1 litre with that reagent. The concentration of this solution is 600 parts of calcium per million. A 60-p.p.m. standard solution is prepared by suitable dilution with acetate reagent.

PROCEDURE

*Preparation of the extract*—Prepare the extract by treating 10 g. of finely chopped fresh plant tissue with 200 ml. of acetate reagent in a Waring blendor and decolorising with 1 g. of purified carbon (not bone charcoal). After 3 minutes, filter the extract through a No. 42 Whatman filter-paper. (Extracts of dry material can be prepared by shaking 1 g. of dry matter with 100 ml. acetate reagent (1) in a to-and-fro shaker for 1 hour, and then clarifying and filtering as above.)

*The extract volume*—The standard extract volume is 10 ml. Place this volume in a 25-ml. centrifuge tube. (The volume of extract taken should contain between 0·05 mg. and 0·6 mg. of calcium. For samples containing greater amounts of calcium a suitable volume is diluted to 10 ml. with acetate reagent.)

*Precipitation of calcium*—Heat the centrifuge tube containing the extract volume in a water-bath to a temperature of 80° to 90° C. Add 1 drop of methyl red indicator, followed by 2 ml. of warm oxalate reagent (2). Add diluted aqueous ammonia (1 in 4) drop by drop until the acidity is nearly neutralised and the solution is faintly acid. Mix the contents of the tube thoroughly by rotating it between the hands. Allow to stand for an hour before centrifuging.

*Washing the precipitate*—Centrifuge the contents of tube at 3000 r.p.m. for 10 minutes. Suck off the supernatant liquid by means of a fine-bore glass tube connected to a water pump. Remove excess of oxalate and acetate reagents by two washings with the wash solution (3).

*Drying the precipitate*—After washing the precipitate, place the tubes in an electric oven at 90° C. till dry. Avoid over-heating.

*Development of colour*—Add 1 ml. of the hydrochloric acid reagent (4), accurately measured, to each tube and dissolve the precipitate completely by shaking the tube. If the precipitate is difficult to dissolve the tube can be placed in a water-bath for 2 or 3 minutes. Add 10 ml. of the thiocyanate reagent (7) and mix thoroughly. Allow the colours to develop for 30 minutes. It is convenient to develop colours in 20 to 25 tubes at a time.

*Measurement of colour intensity*—Measure the intensity of the colour by means of a Spekker absorptiometer. Use the 1-cm. cell, heat filters H503 and green filters No. 5. Set the drum at 1·00 against distilled water.

*Calibration*—Take 2, 4, 6, 8 and 10 ml. of the 60-p.p.m. calcium standard in centrifuge tubes, make up to 10 ml. with acetate reagent and treat as described above. Re-calibration is required when new potassium thiocyanate, ferric chloride or hydrochloric acid solutions are prepared.

NOTES—

*Range of the method*—When the concentration of calcium ions in the extract volume (10 ml.) is greater than 60 parts per million inaccurate results are obtained. If the concentration is between 60 and 120 p.p.m., the colours may be adjusted by the addition of a further 1 ml. of reagent (4) and 10 ml. of reagent (7). It may also be possible to measure higher concentrations of calcium by altering the strength of the thiocyanate reagent. This however has not been found necessary for most plant extracts. For extracts containing more than 60 p.p.m., a suitable aliquot is diluted to the extract volume with acetate reagent. The method is therefore capable of measuring concentrations of calcium of from 10 to 600 p.p.m.

*Precipitation of calcium*—Under the conditions of precipitation calcium is precipitated quantitatively. In the presence of excess of ammonium oxalate, magnesium ions in the extract do not interfere. The method has been tested with concentrations of magnesium higher than are normally found in plant extracts but no error resulted in the determination of calcium (Table I). The precipitation is usually complete within half an hour (Table II), but it is convenient to standardise the time at 1 hour.

TABLE I

THE EFFECT OF MAGNESIUM

| Concentration, p.p.m. | | Spekker reading (average of three determinations) |
|---|---|---|
| Calcium | Magnesium | |
| 12 | — | 0·205 |
| 12 | 6 | 0·205 |
| 12 | 20 | 0·200 |
| 12 | 160 | 0·210 |
| 36 | — | 0·510 |
| 36 | 80 | 0·510 |

TABLE II

THE EFFECT OF PRECIPITATION TIME

| Concentration of calcium, p.p.m. | Time between precipitating and centrifuging | Spekker reading |
|---|---|---|
| 12 | 10 min. | 0·185 |
| 60 | 10 " | 0·765 |
| 12 | 20 min. | 0·190 |
| 60 | 20 " | 0·765 |
| 12 | 30 min. | 0·195 |
| 60 | 30 " | 0·780 |
| 12 | 1 hour | 0·205 |
| 60 | 1 " | 0·790 |
| 12 | 2 hours | 0·205 |
| 60 | 2 " | 0·785 |
| 12 | 18 hours | 0·205 |
| 60 | 18 " | 0·785 |

*Washing the precipitate*—Thorough washing of the precipitate is essential if accurate results are to be obtained. The wash solution recommended by Le Fevre and Nicholson[2] was found to be satisfactory and much superior to washing with dilute ammonia, alcohol and ether. The latter technique required three washings and four centrifugings, which make it a long, tedious process. Inaccurate results were obtained owing to the difficulties of centrifuging the calcium oxalate precipitate from these liquids. Two washings with the "wash solution" (3) were found to be satisfactory. Furthermore, solution (3) gives a suspension which is easily centrifuged at 3000 r.p.m.

*The effect of acidity on intensity of colour*—With increasing concentration of hydrochloric acid in the final solution, the sensitivity of the method is decreased (Table III). Various concentrations of hydrochloric acid were tried for dissolving the calcium oxalate precipitate. Reagent (4), 5 per cent. v/v hydrochloric acid gave the most satisfactory range of colours. With concentrations below this, difficulty was experienced in dissolving the precipitate.

The concentration of ferric thiocyanate was chosen to give a suitable range of Spekker readings under the conditions of the method. This was found to be 0·08 per cent. of potassium thiocyanate and 0·04 per cent. of ferric chloride, which gives a Spekker reading of about 0·04 in the absence of calcium and 0·75 with 60 p.p.m. of calcium in the extract volume.

The graph of calcium concentration against the Spekker drum reading is linear up to approximately 0·7. With increasing calcium concentration above this point, the reduction

in colour becomes less rapid and the graph curves rapidly, owing to interference by the yellowish colour of reduced iron thiocyanate.

The sensitivity of the method is increased by increasing the proportion of potassium thiocyanate to ferric chloride. A point is reached, however, at which further increases cause a serious reduction in the range of the method. The concentration of potassium thiocyanate

TABLE III

THE EFFECT OF HYDROCHLORIC ACID

| Concentration of "concentrated" hydrochloric acid (v/v), % | Concentration of calcium in extract volume, p.p.m. | Spekker reading | Difference |
|---|---|---|---|
| 5 | 12 | 0·205 | 0·585 |
| | 60 | 0·790 | |
| 10 | 12 | 0·255 | 0·490 |
| | 60 | 0·745 | |
| 15 | 12 | 0·315 | 0·415 |
| | 60 | 0·730 | |
| 20 | 12 | 0·350 | 0·365 |
| | 60 | 0·715 | |

and of ferric chloride prescribed for reagent (7) was found to give the maximum sensitivity for the range of calcium concentration required in this method.

*Development of colour*—The development of the thiocyanate colour is almost instantaneous, but it is advisable to allow the solutions to stand for several minutes in order to ensure that equilibrium has been reached. It was found convenient to read the colours half an hour after development. The colours are stable up to 1½ hours after development.

## RESULTS

The method was checked by determining the calcium contents of typical plant extracts; a known amount of calcium was then added to fresh samples of each extract and the calcium contents re-determined. The percentage recovery of calcium was calculated and was found to be satisfactory (Table IV). In addition some acetate extracts of plant tissue were made and the calcium concentration in each determined in 5 ml. and in 10 ml. of the extract. Agreement was good; the results for four samples are shown in Table V.

TABLE IV

THE RECOVERY OF CALCIUM

| | Calcium in extract volume, mg. | | | Calcium added, mg. | | |
|---|---|---|---|---|---|---|
| Extract | Determined | Originally present plus amount added (calculated) | Re-determined | Known | Determined | Difference as % of the amount added |
| 1 | 0·452 | 0·572 | 0·572 | 0·12 | 0·12 | — |
| 2 | 0·399 | 0·519 | 0·522 | 0·12 | 0·123 | +2·5 |
| 3 | 0·259 | 0·499 | 0·495 | 0·24 | 0·236 | −1·7 |

The accuracy of the method was also tested by comparison with the standard volumetric procedure of titrating the calcium oxalate with standard potassium permanganate solution

TABLE V

THE DETERMINATION OF CALCIUM IN 5 AND 10 ML. OF EXTRACT

Results for four samples

| Volume of extract used | Concentration (p.p.m.) of calcium in extract volume (determined) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| 5 ml. .. .. | 46·0 | 39·6 | 36·2 | 41·2 |
| 10 ml. .. .. | 45·2 | 39·0 | 36·4 | 39·9 |
| Difference, % .. | 1·7 | 1·5 | 0·55 | 2·9 |

(Table VI). Eleven typical plant extracts were used for this comparison. The values obtained by the two methods were in close agreement. The coefficient of correlation was found to be +0·996.

TABLE VI

COMPARISON OF THE COLORIMETRIC METHOD AND VOLUMETRIC POTASSIUM PERMANGANATE METHOD

| Sample | Concentration of calcium, mg. per 100 ml. | |
|---|---|---|
| | Thiocyanate | Permanganate |
| 1 | 5·20 | 5·30 |
| 2 | 8·30 | 8·28 |
| 3 | 9·88 | 9·92 |
| 4 | 11·56 | 11·58 |
| 5 | 15·12 | 15·12 |
| 6 | 10·00 | 9·98 |
| 7 | 7·04 | 7·14 |
| 8 | 7·12 | 7·04 |
| 9 | 19·32 | 19·38 |
| 10 | 14·84 | 14·80 |
| 11 | 8·96 | 8·88 |
| Mean | 10·67 | 10·67 |

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# A New Type of Polarographic Cell Suitable for Routine and Research

BY G. S. SMITH

SYNOPSIS—A flow-through type of polarographic cell, suitable for universal use, is described. It embodies an external anode with a simple liquid junction, provision for de-oxygenation of electrolytes in the absence of mercury, and means for determining the capillary characteristics.

NEARLY all the various types of cells used in polarography fail to satisfy one or more of the following desirable requirements.

(*a*) An external anode should be used to ensure that the anode potential is independent of the nature of the solution being analysed, and also, incidentally, to prevent wastage of pure mercury.

(*b*) When an external anode is used, the junction should be simple to establish and maintain, the anode solution should not contaminate the electrolyte in the cell, or be contaminated by it, and the resistance of the junction to electric current should be negligible.

(*c*) Removal of dissolved oxygen by means of the passage of an inert gas should be capable of being carried out in the cell itself in the absence of mercury in order to avoid dissolution of traces of mercury. Afterwards the surface of the liquid should not be allowed to come into contact with oxygen of the air.

(*d*) It should be possible to fill and empty the cell, and to wash it adequately, with a minimum of manipulation; thus, some form of flow-through cell is desirable.

(*e*) Simple means of weighing the mercury drops forming in the actual solutions used should be available, so that from the rate of flow and the drop-time the characteristics of the

capillary may be calculated, and the results of diffusion-current measurements may be compared, when necessary, with those obtained with other capillaries.

(*f*) The apparatus should be maintained at a constant temperature.

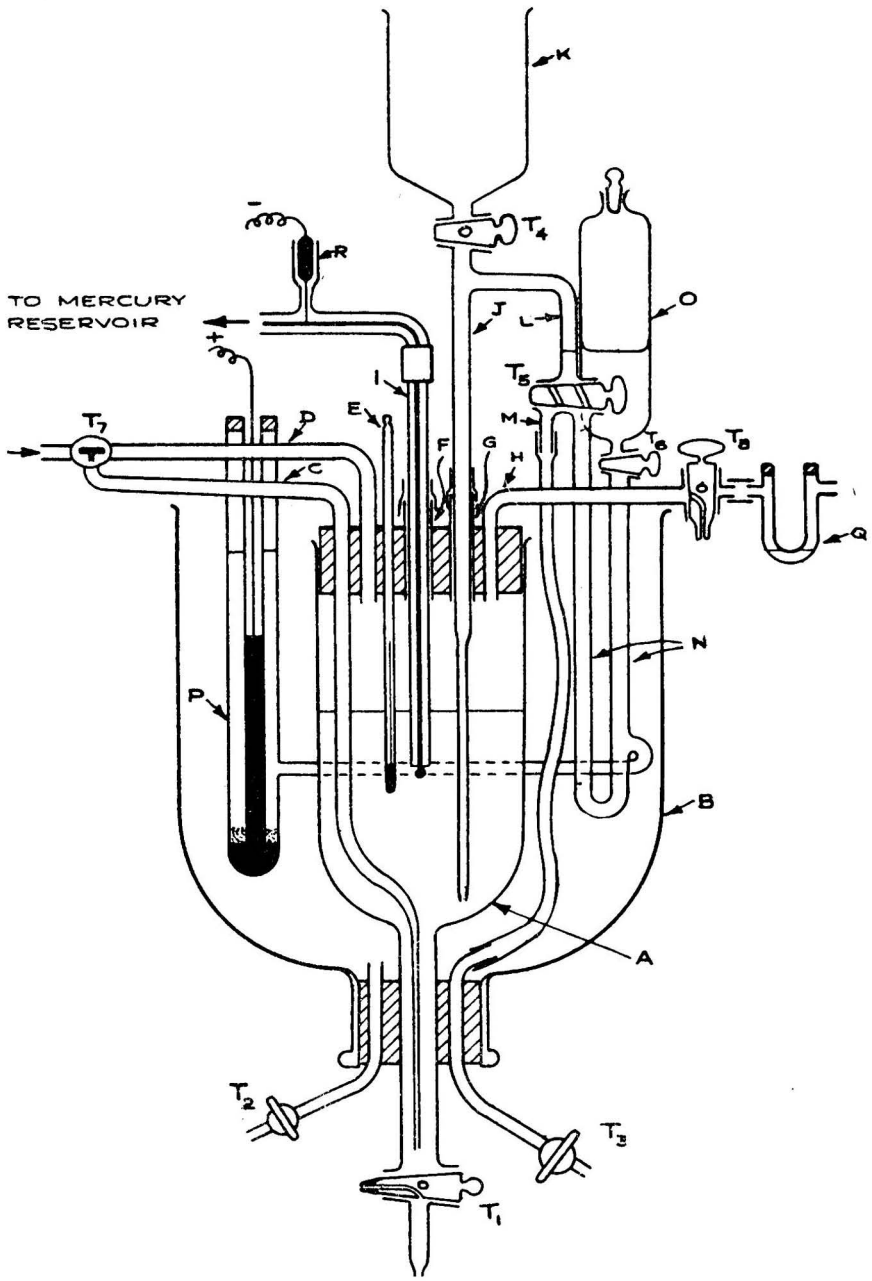


Fig. 1. Cell for polarography.

With these objects in view the apparatus described below was constructed. Its complexity is only apparent since all the operations with it are very simple and are rapidly carried out.

DESCRIPTION OF THE APPARATUS—

The apparatus is shown diagrammatically in Fig. 1. The cell, A, is a Gooch crucible adaptor with a tap $T_1$ fused on to the stem. $T_1$ has a direct outlet and another outlet along the barrel. The stem of the cell passes through a split and re-sealed rubber bung held in the neck of a reagent bottle which has been cut off about half-way up the sides and inverted to act as a water-bath, B. This bung carries two other tubes with taps: $T_2$ is for emptying the water-bath, and $T_3$, which is normally left open, is an outflow for washings of the liquid-junction tube (see below). The top of the cell is fitted with a rubber bung with six holes through which pass tubes C and D for the inlet of nitrogen, a thermometer E, short tubes F and G for insertion of the capillary, I, and solution-delivery tube J, and finally the gas outlet tube, H. Tubes F and G are fitted with rubber sleeves, and I and J are slightly enlarged at suitable points so that they make air-tight seals with these rubber sleeves, but otherwise can be passed freely in or out of the outer tubes. The lower part of J is drawn off slightly. Normally, J and the parts connected to it do not require removal.

The solution-delivery tube J, delivery funnel K with tap $T_4$, liquid-junction tube L, tap $T_5$, outlet tube M, connection tubes N to reservoir O (containing 3·5 *M* potassium chloride), through tap $T_6$, and to calomel electrode P, are entirely glass with no intermediate rubber connections. Tube M is joined to the outlet tap $T_3$ by rubber tubing. The gas inlet tubes C and D are connected to a three-way tap $T_7$, the other side of the tap being connected through a safety bottle and washing bottles to a cylinder of nitrogen. Tube D terminates just below the rubber bung, but tube C continues to the bottom of the cell just above tap $T_1$ and it is drawn off to a point so that fine bubbles of gas can be passed through a solution in the cell when tap $T_7$ is suitably turned. The gas outlet tube H is connected to a tap $T_8$ which can be turned so as to allow gas to pass out through the barrel or through a bubbling tube Q, or, when necessary, to stop the outflow of gas altogether.

The mercury capillary I is joined by means of plastic tubing to a capillary tube fitted with a fused-in platinum wire leading to mercury in the cup R for the cathode connection. The other end of the capillary tube is connected to a mercury reservoir. The calomel electrode is the anode; it contains mercury covered by a layer of calomel and 3·5 *M* potassium chloride, and connection to the mercury is made through a platinum wire in the inner tube which is held by a bung at the top of tube P. Between the electrode and reservoir O, and also in the connecting tube to tap $T_5$, there is a continuous column of 3·5 *M* potassium chloride.

OPERATION—

*Filling the cell*—The solution to be examined is placed in the delivery funnel, K, and allowed to run into the cell through the tap $T_4$. At the same time tap $T_5$ is turned momentarily so that some of the liquid passes through the tap and then out through tube M and tap $T_3$. Tap $T_4$ is then turned off so that a continuous column of liquid occupies the tubes J and L.

*Removal of oxygen*—With a glass stopper, instead of the mercury capillary, inserted in the rubber sleeve of tube F, nitrogen gas is passed through C for several minutes, the gas escaping through tap $T_8$. The capillary is then inserted, tap $T_8$ is turned so that no gas can escape, and tap $T_5$ is turned so that the excess pressure in the cell drives some of the liquid up through J and out through $T_3$, thus ensuring that de-oxygenated liquid is present in J. Nitrogen is then passed for a few minutes longer with tap $T_5$ closed and tap $T_8$ open. Tap $T_7$ is then turned so that gas passes over the surface of the liquid in the cell and out through the barrel of tap $T_8$.

*Establishment of liquid junction*—With the stopper of O removed, tap $T_6$ is opened, and tap $T_5$ is gently turned so that a column of the dense potassium chloride solution rises slowly in tube L. Tap $T_6$ is then turned off, and the stopper of O is inserted. $T_5$ is fully opened and left in this state until the polarogram has been obtained. A somewhat similar method of obtaining a liquid junction, but for another purpose, has been described by Coates.[1]

*Emptying and washing the cell*—Tap $T_5$ is first turned off, taps $T_1$ and $T_4$ are turned so that the liquid flows out of the cell, tap $T_5$ is then turned so that the liquid in tube L flows out through M and $T_3$, and $T_7$ is turned so that the liquid in tube C is forced out. The cell and tubes are washed by pouring water in the tap funnel K and allowing it to flow through L and J, taps $T_5$ and $T_3$, and $T_1$.

*Weighing of mercury drops*—When it is desired to determine the drop weight or the rate of flow of mercury, 10 or 20 drops of mercury are allowed to collect at the bottom of the cell. The mercury, together with a small amount of the electrolyte, is then run out through

tap $T_1$ into a special tube as shown in Fig. 2. The mercury in the tube is washed several times with water and the washings are poured off through the side tube. It is then washed with alcohol, and finally with ether, and the globule, together with the small amount of

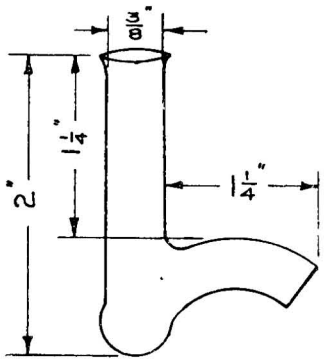


Fig. 2. Washing tube for mercury drops.

ether that cannot be removed by pouring, is tipped into a paper capsule obtained by cutting off the upper two-thirds of a Soxhlet thimble. The globule is swirled round inside the capsule once or twice to remove the ether by absorption and evaporation, then tipped on to a counterpoised watch-glass on a balance pan, and weighed immediately.

GENERAL REMARKS—

The dimensions of the cell, etc., may, of course, be chosen to suit the work of a particular laboratory. The capacity of the original cell was about 100 ml., and that of the delivery funnel was about 50 ml. The connecting tubes consisted of ordinary $\frac{1}{4}$-inch diameter glass tubing. The reservoir for the potassium chloride solution was of 25-ml. capacity, and the level of liquid therein was kept below the level of the horizontal part of tube L to avoid the risk of the solution flowing into the cell when taps $T_6$ and $T_5$ were opened.

The same cell may be used for the analysis of very small volumes, possibly single drops, if an internal anode is used. For this the mercury capillary is made long enough to reach into the stem of the cell and the side outlet of tap $T_1$ is connected to a small mercury reservoir with an anode connection. This tap is turned so that a small amount of mercury is allowed to run into the empty cell. Another turn of the tap allows the mercury to run out of the cell but leaves a column of mercury in the longitudinal bore of the tap, and another slight turn seals the cell without allowing any more mercury to run in. The liquid to be analysed is introduced into the stem of the cell through the opening G usually used for the delivery tube. Nitrogen is then passed through to remove oxygen, and tap $T_1$ is turned so that mercury rises in the stem and forces up the liquid until it comes in contact with the capillary. The apparatus is then ready for the taking of the polarogram.

This paper is published by permission of the Ministry of Supply and the Controller of H.M. Stationery Office. The apparatus described forms part of the subject-matter of Provisional Patent Specification No. 5634/49, dated 1st March, 1949.

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# Notes

## A NOTE ON THE SEPARATION OF MIXTURES OF ADIPIC AND SEBACIC ACIDS

THE separation of a mixture of acids into its component acids is a problem that frequently occurs in analytical chemistry. A method of separating such mixtures has been proposed by Brancker.[1] The essential point of the method is that alkali is added to the stoichiometric end-point of the strongest acid in an aqueous solution in contact with a suitable solvent. The weaker acids are not neutralised by the alkali and so are in the un-ionised form which will be distributed between the solvent and the water. The strong acid, however, is almost completely neutralised and so remains mostly in the aqueous phase. By this "stoichiometric extraction" Brancker claims that a mixture can be resolved into its component acids. Brancker's paper is theoretical and contains no practical proof of the method. Recently, however, Clasper and Haslam[2] separated a mixture of sebacic and adipic acids by a method similar to that suggested by Brancker using ether as the solvent. Analysts might conclude that the simple method proposed by Brancker is likely to be more useful in separating acids than more elaborate methods such as "dissociation extraction."[3] It must be pointed out, however, that Brancker's method is not efficient unless the acids in the mixture have widely different dissociation constants. He himself seems to be unaware of this fact, apparently owing to his use of "degree of dissociation" which makes the theory difficult to handle and to understand.

It will be shown below that the separation of adipic and sebacic acids achieved by Clasper and Haslam is much greater than can be explained by stoichiometric extraction, but that it is due to preferential solvent extraction of the sebacic acid into the ether phase. The addition of alkali to the stoichiometric end-point of the adipic acid does not give the best separation.

It will be convenient first to outline the theory in terms of dissociation constants using the same assumptions made by Brancker, namely that only the undissociated acid is distributed between the solvent and the water, that corrections for activity coefficients are negligible and that there is no association of acids in the solvent phase.

If adipic and sebacic acids are represented by $H_2A$ and $H_2Sb$ respectively, we have the following equilibria—

$$H_2A \rightleftharpoons HA^- + H^+ \qquad K_1 = 3{\cdot}8 \times 10^{-5} \text{ at } 25^\circ \text{ C.}$$
$$HA^- \rightleftharpoons A^{--} + H^+ \qquad \phi_1 = 2{\cdot}4 \times 10^{-6} \text{ at } 25^\circ \text{ C.}$$
$$H_2Sb \rightleftharpoons HSb^- = H^+ \qquad K_2 = 2{\cdot}6 \times 10^{-5} \text{ at } 25^\circ \text{ C.}$$
$$HSb^- \rightleftharpoons Sb^{--} + H^+ \qquad \phi_2 = 2{\cdot}6 \times 10^{-6} \text{ at } 100^\circ \text{ C.}$$

The values quoted for the dissociation constants are taken from Heilbron.[4] It will not seriously affect the argument if we put $\phi_1 = \phi_2$.

If $Va$ is the volume of the aqueous phase,

$Vs$ is the volume of the solvent phase,

$D_1$, $D_2$ are the partition coefficients of the undissociated adipic and sebacic acids respectively.

A, S are the total amounts of adipic and sebacic acids respectively,

$x$ is the hydrogen ion concentration,

subscripts $aq$, $s$ refer to the aqueous and solvent phases respectively,

then we have that:

$$A = Va[H_2A]_{aq} + Va[HA^-] + Va[A^{--}] + Vs[H_2A]_s \quad .. \quad .. \quad .. \quad (1)$$

*i.e.*,

$$A = Va[H_2A]_{aq}\left\{1 + \frac{K_1}{x}\left(1 + \frac{\phi}{x}\right) + \frac{Vs}{Va} D_1\right\} \quad .. \quad .. \quad .. \quad (2)$$

A similar expression holds for sebacic acid, whence we get—

$$\frac{[H_2Sb]_s}{[H_2A]_s} = \frac{D_2S}{D_1A} \cdot \frac{\left\{1 + \beta_1 + \frac{Vs}{Va} D_1\right\}}{\left\{1 + \beta_2 + \frac{Vs}{Va} D_2\right\}} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where $\beta_1 = \frac{K_1}{x}\left(1 + \frac{\phi}{x}\right)$ and similarly for $\beta_2$.

If we add $b$ mols. of base BOH to the system, assuming that the salts formed are completely dissociated, we have—

$$[B^+] + [H^+] = [HA^-] + [A^{--}] + [HSb^-] + [Sb^{--}] + [OH^-]$$

$$i.e., \quad \frac{b}{Va} + x - [OH^-] = \frac{A\beta_1}{Va\left\{1 + \beta_1 + \frac{Vs}{Va}D_1\right\}} + \frac{S\beta_2}{Va\left\{1 + \beta_2 + \frac{Vs}{Va}D_2\right\}} \quad .. \quad (4)$$

From equation (3) it follows that the maximum value of $\frac{[H_2Sb]_s}{[H_2A]_s}$ is given by $\frac{D_2S}{D_1A} \cdot \frac{K_1}{K_2}$. If there is no *solvent* extraction effect, *i.e.*, if $D_2 = D_1$, and if the mixture originally contained 50 per cent. sebacic acid, then the maximum proportion of the sebacic acid in the mixture can be calculated to be 60 per cent. This will be when $\beta \gg \left(1 + \frac{Vs}{Va} D\right)$, *i.e.*, at high pH values when the total amount of acid carried by the solvent is small.

The fact that Clasper and Haslam achieved a separation of the acids is due to the fact that $D_2 \gg D_1$ and not to any effect of stoichiometric extraction.

The fact that $D_2 \gg D_1$ can be seen from Fig. 2 of Clasper and Haslam's paper, where the total amount of acid in the aqueous phase is plotted against the composition of the mixture of acids. When pure adipic acid was used, most of the acid was in the aqueous phase; on the contrary, most of the sebacic acid was in the solvent phase when pure sebacic acid was used. Indeed, the data of Clasper and Haslam can be used to calculate the partition coefficients of the acids. It can be shown that when the acids alone are shaken with water the pH is low enough for most of the acid to be in the undissociated form. When 0·500 g. of adipic acid was shaken with 50 ml. of water and 35 ml. of ether, the acid in the aqueous phase was equivalent to $2 \times 24{\cdot}12$ ml. of 0·1 $N$ sodium hydroxide solution, *i.e.*, 0·354 g. of adipic acid.

The partition coefficient of adipic acid between ether and water is given by

$$D_1 = \frac{(0{\cdot}500 - 0{\cdot}354)}{35} \times \frac{50}{0{\cdot}354} = 0{\cdot}6$$

The partition coefficient of sebacic acid between ether and water is given by a similar calculation as 50. These values of the partition coefficients will be subject to correction due to the mutual solubility of the phases. The correction will be ignored, however, in the following calculations which will be insensitive to relatively small corrections in the partition coefficients.

A′, the total adipic acid in the aqueous phase can easily be shown to be given by

$$A' = \frac{A(1 + \beta)}{1 + \beta + \frac{Vs}{Va}D_1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

and the total adipic acid in the solvent phase is equal to (A − A′). Similar equations hold for the sebacic acid. We can thus calculate the total acid and also the composition of the acids contained in the aqueous and solvent phases, for various values of $\beta$. The values of $b$/A corresponding to these values of $\beta$ can be obtained by solving equation (4), putting $\beta_1 = \beta_2$. In this way Table I has been constructed for the case where A = S.

TABLE I

| $b$/A | Total acid in aqueous phase, divided by A | Adipic acid in aqueous phase, % | Total acid in solvent phase, divided by A | Sebacic acid in solvent phase, % |
|---|---|---|---|---|
| 0 | 0·73 | 96 | 1·27 | 77 |
| 0·5 | 0·91 | 93 | 1·09 | 90 |
| 1·0 | 1·14 | 84 | 0·86 | 95 |
| 1·5 | 1·55 | 65 | 0·45 | 99 |
| 2·0 | 2·00 | 50 | 0 | 100 |

From Table I it can be seen that a considerable separation of adipic and sebacic acids is theoretically predicted although, since we have assumed $K_1 = K_2$, no stoichiometric extraction effect is possible for this calculated case. It can also be seen that as the total amount of alkali tends to the amount equivalent to the total acid present (*i.e.*, $b$/A tends to 2), the acid in the solvent

phase tends to be pure sebacic acid. The total amount of acid present in the solvent phase, however, decreases as $b/A$ increases. The best separation will therefore be achieved by extracting the mixture many times at a high pH value, so that at each extraction the ether phase removes nearly pure sebacic acid. This is the basis of the separation achieved by Clasper and Haslam in their continuous extraction apparatus. The effect is due to solvent extraction however and not to stoichiometric extraction. If $D_2$ were not much greater than $D_1$, an elaborate technique would be required to separate the acids.

In order to check these conclusions, an experiment was carried out for the case $b/A = 1$. 0·389 g. of adipic acid (equivalent weight 73·0) was neutralised by sodium hydroxide to the end-point of phenolphthalein and the volume made up to 50 ml. 0·531 g. of recrystallised sebacic acid (equivalent weight 102·0) was added, together with 35 ml. of ether and the mixture was shaken at 20° C. for 30 minutes. The aqueous phase was removed and an aliquot titrated. Two experiments gave the result that the excess acidity in the aqueous layer was 23 and 24 per cent. of the total adipic acid present. From Table I when $b/A = 1$, the excess acidity is expected to be 14 per cent. This acidity can only be due to the sebacic acid so that the aqueous phase will not contain adipic acid purer than 82 per cent. Samples of acids obtained from the aqueous and the ether phases were examined qualitatively in the infra-red and it was found that the acid from the aqueous phase was mainly adipic acid contaminated by a considerable quantity of sebacic acid, and the acid from the ether phase was sebacic acid contaminated by adipic acid. In view of the assumptions made in the calculations for Table I the agreement between the experimental data and the calculated value can be regarded as satisfactory, clearly showing that it is not possible to separate completely a mixture of adipic and sebacic acids by a single extraction at $b/A = 1$.

I am grateful to Mr. A. R. Philpotts for the infra-red analyses and to the Directors of the Distillers Company Limited for permission to publish this note.

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4. Heilbron, "Dictionary of Organic Compounds," Eyre & Spottiswoode, Ltd., London, 1937.

THE DISTILLERS COMPANY LTD.
RESEARCH AND DEVELOPMENT DEPARTMENT
GREAT BURGH, EPSOM

W. S. WISE
*September*, 1949

## THE COLORIMETRIC DETERMINATION OF ALDEHYDE IN DISTILLED LIQUORS

THE procedures described in the A.O.A.C.[1] and in Scott[2] for the colorimetric estimation of aldehyde in alcoholic beverages did not give satisfactory results when applied to the routine analysis of brandy. The agreement between duplicate samples was poor, the discrepancy often exceeding 10 per cent.

The method was checked and it was found that the difference in behaviour of the standard solution compared with that of the sample with respect to colour development was an underlying cause for producing fluctuating results.

In Fig. 1 the intensity of colour is plotted against the time allowed for colour development. The difference between the behaviour of the standard solution (10 parts of acetaldehyde per 100,000) and a brandy sample is clearly seen. The standard solution increases in intensity at a very high rate whereas, in comparison, the brandy sample undergoes very little darkening in colour. The A.O.A.C. and Scott recommend reading the colour 15 minutes after the addition of the fuchsin - sulphite reagent, but because of the great divergence between the curves every second that passes means that the sample is being compared with a standard of rapidly increasing intensity. This behaviour of the standard solution makes it virtually impossible to obtain good agreement between duplicate samples.

It was felt that if the rate of increase of the intensity of the standard solution could be greatly reduced, the value of the method would be considerably enhanced. The standard solution, although made up in 50 per cent. v/v alcohol, differs from the brandy sample in that it does not contain small quantities of acetic acid, esters, furfural and fusel oil. Any one or a combination of these substances is probably responsible for preventing the increase in intensity of the colour of the

sample. When acetic acid is incorporated in the standard aldehyde solution at a concentration of 16 parts per 100,000, which approximates to its level in a brandy, the rate of increase of colour intensity with time is reduced to about one-third of its former value. The curve is shown in Fig. 1.

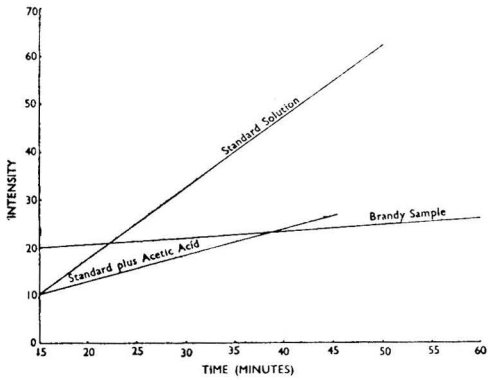


Fig. 1.

The simple expedient of incorporating acetic acid in the standard solution is therefore recommended. Further improvement in the method is made possible by preparing a separate standard for each sample and suitably staggering the addition of the fuchsin - sulphite reagent to each pair of tubes.

The authors wish to thank the management of the Castle Wine and Brandy Company for permission to publish this note.

### References

1. "A.O.A.C.," 6th Ed., 1945, p. 194.
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L. Gorfinkel
G. S. Skelton
Castle Wine and Brandy Company Laboratories
Cape Town

*August*, 1949

## PRESSURE COOKING AS AN AID IN THE ISOLATION OF EXTRANEOUS MATTERS IN CEREAL PRODUCTS

It has been found that by using a pressure cooker the acid digestion stage in the method for the extraction of extraneous matters present in wheaten flour and biscuits[1,2] is facilitated. A household pressure cooker, fitted with a pressure gauge, large enough to hold at least two 800-ml. squat beakers is convenient, but any other closed heating vessel fitted with a pressure gauge, *e.g.*, a steriliser or autoclave, should serve.

Pressure cooking obviates the following disadvantages of the ordinary digestion: the varying time taken for the pasty admixture of acid and cereal product to come to boiling-point, the risk of local overheating and charring and the labour of manual stirring up to and during the boiling period. Its advantages are that two tests at least are digested simultaneously, so that tests on duplicate samples receive the same heat-treatment and the product subsequently shows much less "dross" at the interface of the petrol and aqueous layers. The method should be adaptable for the treatment of other cereal products. There has been no evidence that hairs or insect fragments are disintegrated by the use of a higher temperature.

### Procedure

Extract the fat from a quarter of a pound or 100 g. of the powdered biscuits or cereal product with light petroleum (b.p. 40° to 60° C.) and dry the residue. Wheaten flour does not require extraction. Place the dry material in a 800-ml. squat beaker and stir in boiling 0·5 *N* hydrochloric acid. Flour or biscuits of low fat content require 400 ml. of acid, but for shortened biscuits 300 ml. are sufficient. Put 300 ml. of distilled water into the cooker and stand the beakers upon a metal platform. Close the lid of the cooker and raise the temperature of the water to boiling-point with the escape-valve open to allow of the free passage of air; it is important that no pressure

builds up while air is being displaced. When all the air has been driven out by the steam, close the escape-valve and raise the pressure, slowly and steadily, to 20 lb. per square inch and maintain this pressure for 10 minutes. There is a risk of the contents of the beakers boiling over if the pressure is raised too rapidly.

Allow the pressure to drop to zero by the gauge, which takes about 20 minutes, before unclamping the lid of the cooker. Remove the beakers, wash down any solids on the sides with hot water and allow to cool. Tests on biscuits are now ready for adjustment to pH for the pancreatin digestion, but flour samples can be extracted for extraneous matters from the acid liquid without further treatment.

For the routine examination of biscuits, a preliminary test has indicated that it may not be necessary to proceed with the pancreatin digestion before the separation of rodent hairs.

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MACFARLANE, LANG & CO., LTD.
IMPERIAL BISCUIT WORKS
OSTERLEY, MIDDLESEX

D. M. FREELAND
*October*, 1949

## A CONSTANT TEMPERATURE BATH OPERATING BELOW ROOM TEMPERATURE

A constant temperature bath has been designed to operate at approximately 20° C. Room temperature is frequently above this, but tap water is almost always available at temperatures of from 8° to 20° C.

The principle adopted was that of a continuous and uniform stream of tap water passing into the bath through a tubular electric heater, and then running to waste. The heater is controlled by a thermostat in the bath itself, and accordingly delivers cold and warmed tap water alternately, so maintaining the bath at a constant temperature.

In the diagram (Fig. 1), which is drawn to scale, tap water enters by the lower side-tube of the vertical tube A, and overflows by the upper tube. This forms a constant-level device, and from it the water flows down the fall tube and up through the heater B, the flow being regulated by a screw clip at the bottom of the heater. It then overflows by the side tube into the open tube E, which forms a convenient sight feed, past the thermometer F, and into the bath G through the tube H, near the front of the bath. It escapes through the overflow J, at the back.

The contact thermometer C can be an ordinary toluene thermo-regulator, but if the bath is to be used continuously, an enclosed-type contact thermometer is better, as the setting is not so likely to be upset by oxidation of the mercury. A contact thermometer of this type may operate at a fixed temperature, or it may be of the Beckmann or other adjustable type. The bath described here is fitted with a 20° C. fixed-contact thermometer, and the results obtained with it are given at the end of this note.

The second contact thermometer D, inside the heater, need only be a very simple affair, with a bulb holding 2 to 3 ml. of mercury, and a stem of 1-mm. bore manometer tubing. Its sole purpose is to prevent damage to the heater if the water supply fails. It is set to operate at about 60° C., and is connected in parallel with C.

The heater consists of about 5 feet of braided heating element, wound on a 2-foot length of 15-mm. glass tubing, and then overwound with several layers of asbestos string. It is designed to take 150 watts.

The relay, R, is of the type that breaks the power circuit when the thermometer makes contact. The enclosed mercury type is recommended, as it will work for long periods without attention. The connections are not shown in detail, as they depend on the type of relay, and details are generally supplied by the makers. Any electrical equipment that satisfies the requirements can be used.

The bath itself is a copper tank, 18 × 15 × 6 inches deep, holding 4½ gallons of water when filled to the overflow. It is designed to take up to 24 samples of jelly in 100-ml. tall beakers, and is fitted with a perforated false bottom for this purpose.

For continuous use, it is convenient to place the bath on a bench or shelf, and to have the glass parts and the relay mounted on a vertical board fixed to the wall. The contact thermometers

are best connected to the relay through plug and socket fittings, so that they can be disconnected and removed if required.

To operate the apparatus, the tap water is regulated so that a slight overflow is maintained from A. The flow through the heater requires regulating according to the prevailing temperature of the tap water because, when the heater is on, the inlet thermometer F must indicate a temperature well above 20° C., *e.g.*, 25° or 30° C.

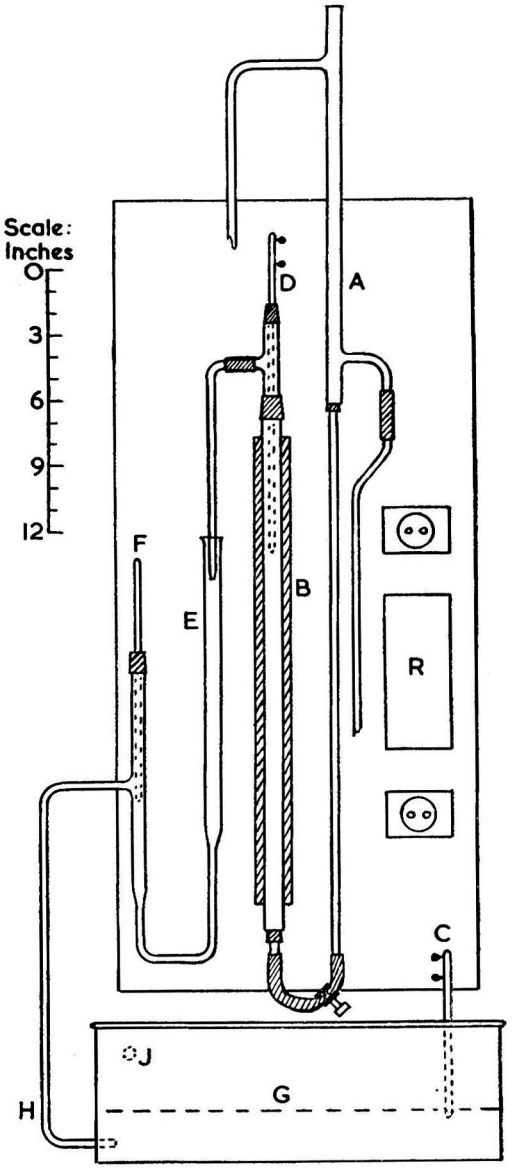


Fig. 1

In routine working, some 20 to 24 beakers of hot jelly are loaded into the bath at once. The temperature rises by about 1·5° or 2° C., but returns to normal after about 1½ hours. The insertion of odd single samples has no appreciable effect on the temperature. When equilibrium is reached, the temperature rises and falls rhythmically as the heater switches on and off. Table I shows the extremes of temperature observed in three widely separated positions in the bath, denoted A, B and C, while running under various conditions.

TABLE I

TEMPERATURE VARIATIONS

| Conditions | | Temperature, ° C. A | B | C |
|---|---|---|---|---|
| Bath empty | Maximum .. .. .. | 19·7 | 19·7 | 19·6 |
| | Minimum .. .. .. | 19·4 | 19·4 | 19·3 |
| Bath containing 12 beakers | Maximum .. | 19·8 | 19·7 | 19·7 |
| | Minimum .. | 19·5 | 19·4 | 19·3 |
| Bath containing 22 beakers | Maximum .. | 19·8 | 19·9 | 19·8 |
| | Minimum .. | 19·4 | 19·6 | 19·3 |

The mean temperature is thus 19·6° C. and the extreme variation ±0·3°. If it is necessary to work exactly to a specified temperature, the use of an adjustable contact thermometer is advisable. This comparatively close regulation without mechanical stirring is probably attributable to the slow circulation caused by the flow of water, and to the shielding effect of the false bottom.

THE LABORATORY
JAMES KEILLER & SON LTD.
TAY WHARF, SILVERTOWN, E.16

O. B. DARBISHIRE
*January*, 1950

# Reviews

ANALYTICAL CHEMISTRY AND CHEMICAL ANALYSIS, 1948. Proceedings of the International Congress on Analytical Chemistry—Utrecht. Pp. vi + 436. New York: Elsevier Publishing Company, Inc. London: Cleaver-Hume Press, Ltd. 1948. Price 25s.

The original of this book appeared as an issue of *Analytica Chimica Acta* (1948, Vol. 2, pp. 419–854) devoted to the International Congress on Analytical Chemistry, held at Utrecht, on June 1st to 3rd, 1948, under the auspices of the Netherlands Chemical Society. The Congress was divided into five sections, and the proceedings consisted of thirteen formal lectures, the presentation of forty-one original papers and four plenary sessions. The book prints in full all the lectures given and papers read in four of the five sections, and the ground covered is indicated by the following resumé.

*Section* 1: *General Methods and Standardisation*—This section includes papers on standardisation, statistical aspects of chemical analysis, the task of the analytical chemist in industry, recent developments in gas analysis, organic elementary analysis, the use of isotopes as tracers, and the mass spectrometer. Of interest to English readers is an account of the present situation in the field of standardisation in the Netherlands and the development there of an organisation dealing with the standardisation of analytical procedures; rules for unification in the description of procedure are given and the necessity of standardising chemical glassware and commonly used apparatus is stressed. Also of considerable interest is a thesis on rationalising analysis; this is summarised in an assertion that the increasing demand for chemical analysis can be met by increasing the productivity per time unit of the scientific analyst, at the same time supplementing untrained people for routine analysis, but even then only with the aid of automatic apparatus.

*Section* 2: *Electrical Methods*—In this section, polarography is represented by papers on modern trends, and the application of polarography to the analysis of products of the metallurgy of zinc and some constituents of glass. The use of electrical methods in industrial problems is briefly discussed; controlled potential electro-analysis is critically considered and a potentiostat and cells for different applications are described. Amperometric titrations and electrical methods for the analysis of water are reviewed. The paper on measurements of the salt content of river water has a considerable outside interest, as it tells of the danger of salt (sea) water rising up the River Maas above the intake for the Rotterdam public water supply, and the resulting necessity to know the movement of the "salt limit." A full description of the self-recording conductivity meter installed for this purpose is given.

*Section* 3: *Emission Spectrography*—The papers read in this section are not included, as they were to be published separately in *Spectrochimica Acta*. This decision would appear to be somewhat unfortunate from our point of view, as the book under review is therefore not a complete record of the proceedings at Utrecht.

*Section 4: Optical Measurements and Physical Methods of Separation*—This section covers reviews and applications of chromatographic and adsorption technique, including analysis of hydrocarbon mixtures; a method for the analysis of hydrocarbon oils by thermal diffusion; a survey of colorimetric and photometric absorption analysis; and applications of infra-red spectrophotometry with particular reference to powders and to vitamin $D_2$. Two fundamental papers deal (*a*) with a research on the influence of reagent concentration in the colorimetric determination of copper, and (*b*) with a spectrophotometric development of Winkler's method for determining oxygen in water, working on the iodine - starch complex, whereby as low a concentration as 0·005 mg. of oxygen per litre can be estimated.

*Section 5: Microbiological Methods and Detection of Traces*—The papers on microbiological work include a general review, estimation of copper, magnesium, molybdenum and lead in plant material and soil, determination of tryptophan, and practical experience in assays using lactic acid bacteria. Trace elements in plants and animals come under review. A claim is made that, by the use of a newly isolated strain of *Aspergillus niger* and an optimal culture solution, the determination of potassium and phosphate in soil by a microbiological method equal in accuracy to chemical methods may be made in one quarter of the time; also that zinc can be determined by this method. A method is given for the determination of sugars in foods by reductiometric and biochemical methods in mixtures that may include fructose, glucose, saccharose, lactose, maltose and dextrins; the results are worked out by what appears to be a somewhat complicated mathematical procedure. New work on estimation of different forms of choline in biological substances concludes the papers in this section; and the book ends with a critical resumé of the work and conferences at the Congress.

This book is valuable as an account of the proceedings of the Congress in Utrecht in 1948. These proceedings established a new status for analytical chemistry. Furthermore, they may well have influenced discussions at the meeting of the International Union of Pure and Applied Chemistry in Amsterdam in 1949, for at that meeting a division of Analytical Chemistry was provisionally arranged, and patronage was accorded to the next Congress of Analytical Chemistry to be held in England in 1952. Preliminary arrangements are now well in hand for this next Congress, and our Society is participating very actively in the preparations, both in respect of membership of Committees and financially. It is hoped that the centre for the meetings will be in Oxford—a pleasing prospect for many of us, and undoubtedly a great attraction for visitors from abroad. With this in mind, the record of the proceedings at Utrecht has an additional value as a background to and guide for the programme for the future event, and therefore may be reconsidered from this point of view.

In the preface, Prof. C. J. Van Nieuwenburg, the President, and Dr. H. A. J. Pieters, the Secretary, present their impressions of the meeting in these words: "We have no doubt that this Congress has clearly shown the great changes analytical chemistry has undergone in recent years. Because of the demand for greater speed and accuracy and the need for handling small quantities of materials the classical methods based on gravimetric and volumetric procedures are rapidly being replaced or supplemented by physico-chemical and physical techniques. The status of analytical chemistry is being raised to a much higher level, and analytical chemistry is becoming a science for the specialist. Modern analysis, with its interests in optical, electrical and microbiological methods, makes very high demands in the training of its practitioners, and it was stressed by speakers from several countries that the training of analytical chemists is a long way behind the requirements of modern industry."

These are impressions by officials recorded when the sense of the meeting was still fresh in mind and are to be accepted as such. But viewed in retrospect by the reader, with the next Congress in mind, other impressions are formed. There would appear to have been an overemphasis on physical methods at the Utrecht meeting. New physical methods or significant developments of such accepted methods should be brought to the attention of analysts immediately or at the earliest possible moment. On the other hand, some physical methods are now fully accepted, and no particular advance in analysis is served by the reiteration of technique to such an extent as to overshadow or even eclipse the fundamental analytical work involved in the procedure. Many physical methods are not substitutes for, but aids to, fundamental chemical analysis. Thus, in one of the papers presented at Utrecht, the problem under attack was the determination of traces of oxygen in boiler water, and the experimental work was concerned with elaboration of Winkler's method where the oxygen present is caused to oxidise a manganous salt and the extent of the oxidation is ultimately assayed by the liberation of an equivalent amount of iodine. A considerable amount of experimental work was undertaken in connection with the

study of the iodine - starch complex and its colorimetric determination. The estimation of the colour is difficult visually, so either a Leifophotometer or a Spekker absorptiometer is used. The paper is entitled: "Spectrophotometric Determination of Traces of Oxygen in Water." An alternative title might well have been: "Determination of Traces of Oxygen in Water by a Modified Winkler Method using the Spectrophotometric Technique for the Colour Estimation of the Starch Iodine Complex." While possibly a cumbersome title it has the great advantage of giving a truer indication of the character of the paper.

Another impression is that reviews occupied a very big proportion of the time of the meeting. Perhaps allowance must be made for the youth, as it were, of the Congress. Reviews serve a vital purpose when the workers in the industries in which analytical methods have application are met together for the first time. Subsequently, however, if such gatherings are resumed at fairly frequent intervals, the necessity for full reviews disappears, and brief summaries of development in the intervals should effectively serve such purposes. There is, however, a clearly defined place for lectures of a review nature by outstanding exponents of, or specialists in, some particular branch of the science.

Finally, there is the question of how far methods should be divorced from the field of application. The Congress is based on methods of analysis. Yet it is often a technical problem which results, after due research, in a new or modified analytical procedure. An instance of this can be cited when the difficulty, arising during the manufacture of penicillin, of determining the moment at which the mould growth should be stopped was resolved by an elegant modification of the paper partition chromatographic technique. To divorce this tale from the account of the relevant details of the manufacture of penicillin would deprive it of a very great interest and possibly of some useful incidental information.

The Netherlands Chemical Society is to be heartily congratulated on sponsoring this momentous meeting. The account of the meeting is admirably presented in *Analytica Chimica Acta*. To all interested in the development of analytical chemistry, this book should be of the greatest interest, and constitute an indispensable reference work. Moreover, as out of the forty-eight addresses and presented papers included in its contents thirteen are in French and no less than thirty-five in English, it is easier for some of us to read than might have been anticipated.

GEORGE TAYLOR

MODERN PLASTICS. By H. BARRON, Ph.D., B.Sc., F.R.I.C., F.I.R.I., F.P.I. Second Edition. Pp. 779. London: Chapman & Hall, Ltd. 1949. Price 50s.

The purpose of this book is to enable the reader with a modest scientific or engineering knowledge to obtain a general view of the plastics industry. The book is divided into six parts: introduction, thermosetting resins and their plastics, cellulose plastics, vinyl plastics, other leading plastics, Nylon, etc., and some important aspects of plastics, *e.g.*, analytical and physical tests.

The general method of treatment of individual resins is to describe the preparation of the raw materials and the resin itself, the chemistry underlying the production of the resin, and its various applications. Although the general field of plastic materials is covered fairly well, it is surprising, in a book of this size, to find no mention of such polymers as terylene and polytetrafluorethylene.

There is plenty of evidence throughout the book of careless proof-reading which should be remedied in future editions. Among the many errors in formulae may be mentioned: *p.* 132, β-resin, *p.* 417, acetylene and vinyl acetylene, *p.* 418, polyvinyl acetal and polyvinyl butyral, *p.* 451, the SH radical, and on *p.* 214, monomethylol urea is described as monomethyl urea.

There are many useful tables in the book giving information about the physical and electrical properties of various plastics and plastic materials. Usually these tables are not referred to at all in the text, and in any event, it would be much better if the original sources of the information were always given.

There is a chapter of 28 pages on the analytical aspects of plastics which is of very doubtful value. Schemes for the examination of miscellaneous plastics are given in detail, but it is improbable that any of these schemes will find widespread use in industry. No mention whatsoever is made of one of the most useful practical schemes of this kind, *i.e.*, that of Shaw (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 541). The analytical details are often quite erroneous, *e.g.*, on p. 704, it is not desirable to test for chlorine after a sodium fusion without taking precautions about the presence of nitrogen or nitrogen and sulphur in the plastic. On p. 710 details are given of the application of the bromide - bromate reaction to the determination of phenols in an aqueous extract without

any reference to the source of the aqueous extract. On p. 712, dealing with urea - formaldehyde resin, we come across the statement—

> "The amount of urea present will be determined by straightforward nitrogen determination using the Kjeldahl method. This has already been described. In this instance 1 c.c. of N/10 acid neutralised = 0·003 gm. nitrogen."

Presumably the factor refers to urea and not to nitrogen. On the same page it should be noted that it is bromine which is used up in oxidising the urea, and the equation given should make this plain.

From the description of the method of determination of the nitrogen content of cellulose nitrate on p. 716, it is obvious that the author of this chapter is not very familiar with the chemistry of the nitrometer method; and the method given on p. 722 for the determination of free stearic acid in calcium stearate is really a method for total stearic acid.

The book is well printed and illustrated and contains a large number of useful references. The price, 50s., is rather high, but despite its many errors and imperfections, this book contains a great deal of information about plastics which is bound to be useful, and particularly so to those chemists without prior knowledge of the subject. J. HASLAM

THE TESTING OF BITUMINOUS MIXTURES. By D. C. BROOME, A.Inst.P., F.Inst.Pet. Second Edition. Pp. viii + 396. London: Edward Arnold & Co. 1949. Price 40s. net.

The appearance of the second edition of this useful volume of the Roadmakers' Library is very welcome, as many advances have been made in the testing of bituminous mixtures since it was first published fifteen years ago. Throughout the author wisely uses the word "bituminous" for coal-tar products as well as for petroleum bitumens. This agrees with international nomenclature, although in some quarters in this country there is a desire to restrict the term.

Unfortunately the chapter on roofing felt has been omitted from the new edition. This material is rapidly gaining in popularity and is finding an ever-increasing field of usefulness. Information regarding the methods of test should be readily available.

There are a few misprints. In the formula at the top of p. 6, the term within the brackets appears to have been inverted, as it was in the first edition. The references to the bibliography numbered 23 and 24 on p. 115 have been transposed, and the whole of the bibliography for "Chapter XV" apparently refers to Chapter XIII. Actually there is no Chapter XV in the book. Near the bottom of p. 247 heat "impact" obviously means input.

The methods of detecting the adulteration of asphalt rock that have been published since the original edition might well have been included, although it is true that they may be found in volume three of the Roadmakers' Library.

These are, however, all minor points. The book is well written and makes excellent reading. The analysis of bituminous materials requires a special technique, and no laboratory which has to deal with such samples can afford to be without a copy. D. M. WILSON

## BIOLOGICAL METHODS GROUP

THE next meeting of the Group will be a Symposium on the Assay of Vitamin $B_{12}$, to be held at 2 p.m. on Tuesday, May 23rd, 1950, at the Medical Society of London, 11, Chandos Street, Cavendish Square, London, W.1. The chair will be taken by Dr. S. K. Kon, and speakers will include Miss M. E. Coates, Dr. W. F. J. Cuthbertson, Mr. H. Pritchard, Mr. G. E. Shaw and Dr. C. C. Ungley.

## PHYSICAL METHODS GROUP

THE 20th Ordinary Meeting of the Physical Methods Group will be held in the meeting rooms of the Iron and Steel Institute, 4, Grosvenor Gardens, London, S.W.1, on Tuesday, May 23rd, at 6.30 p.m. The following papers on Radiochemical Analysis will be read and discussed—"Radiometric assay in tracer research," by F. P. W. Winteringham, A.R.I.C.; "The determination of potash (in fertiliser) by measurement of its radioactivity," by D. S. Lees, B.A., A.Inst.P., W. Broomfield and H. N. Wilson, F.R.I.C.; "Radioactivation analysis—some glimpses of its scope," by A. A. Smales, B.Sc.

ANALYTICAL CHEMIST (male or female) for analysis of cast iron and related material. Previous analytical experience with ferrous alloys an advantage. Apply, stating age, experience and qualifications to:—British Cast Iron Research Association, Alvechurch, Birmingham.

CHEMIST (male), who is primarily interested in analysis, required. Preferably under 30 and of A.R.I.C. or equivalent standard or experience. Applications to Chief Chemist, Spillers Central Laboratory, Station Road, Cambridge, from whom further details may be obtained.

WEST SUFFOLK COUNTY COUNCIL
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APPLICATIONS are invited for the above appointment from persons possessing the qualifications prescribed in the Public Analysts Regulations, 1939, or such other qualifications as the Minister of Food may approve. Applications from persons engaged directly or indirectly in any trade or business connected with the sale of food or drugs in the area of the Authority will not be considered.

The appointment will be subject to the approval of the Minister of Food.

Applications, with details as to qualifications and experience, should be received by the undersigned not later than fourteen days after the date of publication of this advertisement.

L. G. H. MUNSEY,
*Clerk of the County Council.*

Shire Hall,
Bury St. Edmunds.
*28th March*, 1950.

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CORPORATION WATERWORKS

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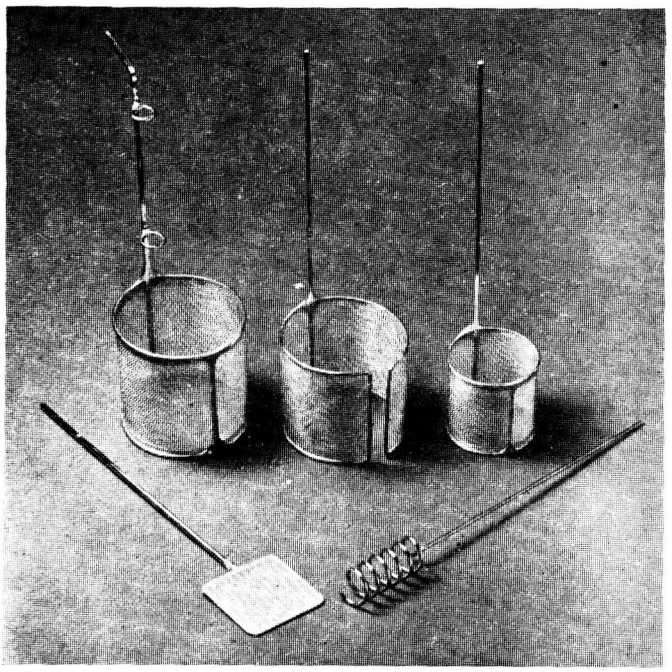
The successful candidate will be required to take charge of the water examination laboratory and to supervise the treatment of supplies and sterilisation of mains, to investigate possible alternative methods of treatment and to advise on the suitability of the various consumable stores used in the Department.

The salary will be in accordance with A.P.T. Grade VI (£595–660).

Applications on forms which can be obtained, together with conditions of appointment, from the Water Engineer and Manager, City Hall, Cardiff, should be returned to the undersigned not later than first post on Thursday, 1st June, 1950.

S. TAPPER JONES, *Town Clerk.*



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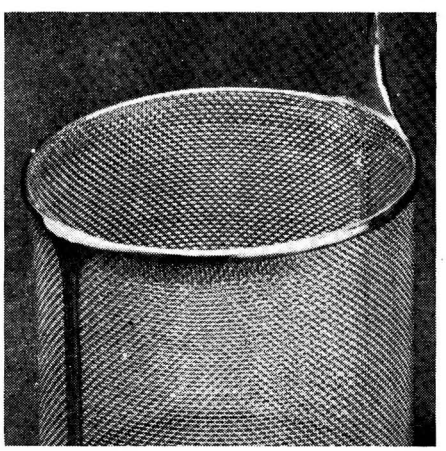

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