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THE ANALYST

EDITORIAL

PROCEEDINGS OF THE FIRST INTERNATIONAL CONGRESS ON ANALYTICAL CHEMISTRY, OXFORD, SEPTEMBER 4TH–9TH, 1952

IN fulfilment of the promise made in the October number of *The Analyst* for last year that a separately bound volume containing the full proceedings, the lectures and the papers presented at the Oxford Congress should be published early in 1953, we are now able to announce that a limited edition of this work has been completed on behalf of the Congress Committee and is ready for publication.

In addition to the matter that has already appeared in the November and December numbers of *The Analyst*, this volume contains a foreword by Sir Robert Robinson, full lists of the various Committees who were responsible under the leadership of Mr. Chirnside for the organisation of the Congress and for administrating its activities in being, and a complete list of the members of Congress.

The three Congress Lectures: "Research in Analytical Instrumentation," by Ralph H. Müller; "The Value and Economic Importance of Chemical Analysis in Industry and Manufacture," by L. H. Lampitt; and "A Contemporary Assessment of the Place of Classical Methods in Chemical Analysis," by C. J. van Nieuwenburg, are reproduced in full.

The scientific papers are grouped by subjects into nine sections: Microchemical Methods, Biological Methods, Electrical Methods, Optical Methods, Radiochemical Methods, Organic Complexes, Presentation of Data, Adsorption and Partition Methods, and General, which includes an important paper on the "Ageing of Crystalline Precipitates" by Professor I. M. Kolthoff.

A catalogue of the Laboratory Demonstrations, with a brief description of the exhibits is included.

Details of the publication are given in a prospectus supplied with this issue.

This book makes the lectures and papers presented at the Congress available to all chemists, whether or not they are members of the Society or subscribers to this journal. It is distinct from the yearly volume of *The Analyst* and complete with its own index, and it forms a valuable and interesting memento of the Oxford Congress—an important event in the history of analytical chemistry.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

DEATHS

We regret to record the deaths of

Francis Clifford Dyche-Teague
Robert Henry Slater.

Analytical Methods Committee

RECOMMENDATIONS OF THE MEAT EXTRACTS SUB-COMMITTEE

Determination of Gelatin in Meat Extract and Meat Stocks

Interim Report

THE Analytical Methods Committee has received the following interim report from the Meat Extracts Sub-Committee, and its publication has been duly authorised.

In the analysis of meat extracts, stocks and allied products, the gelatin content is a valuable guide to the quality and possible admixture or adulteration of the product for both the analyst and the food technologist. Determination of gelatin nitrogen in these products presents exceptional difficulties, and the method generally recommended, which involves precipitation by alcohol, can only yield approximate results. During the Sub-Committee's examination of methods for the analysis of meat extracts and meat stocks, a method for the determination of gelatin, elaborated by Mr. G. Spall in his laboratory, gave promising results and appears to be worthy of further and wider trials. Although the Sub-Committee is still working on this method, particularly with a view to reducing the amount of impurities associated with the gelatin complex, it has been decided to publish details of the method in order to stimulate interested laboratories to do further work on it. The method depends on the formation of a gelatin - formaldehyde complex, nearly insoluble in water, by evaporation of the test solution to dryness in the presence of formalin.

At the time of preparing the Interim Report, the attention of the Sub-Committee was drawn to a private communication by the (then) British Food Manufacturers Research Association (*Food Research*, July, 1929, Vol. 1, No. 4, pp. 92–93), which outlines a method essentially the same as that described below. The fuller investigations carried out by the Sub-Committee amply confirm the results described in this early analytical note.

Method—Weigh 10 g of the extract into a 250-ml beaker and add 125 ml of distilled water. Bring to the boil while stirring constantly and add 0·5 ml of glacial acetic acid. Allow the mixture to digest on a steam-bath for 15 to 30 minutes until the insoluble material has coagulated. Filter through a Whatman No. 4 filter-paper into a 250-ml calibrated flask. Wash well with hot distilled water and after cooling make up to 250 ml. Transfer 25 ml of this solution in a pipette to a porcelain basin (capacity about 190 ml; Royal Worcester, Form 5, No. 4 is suitable). Add 0·25 ml of 40 per cent. formaldehyde solution and mix well. Concentrate the mixture to a thick consistency, add a further 0·25 ml of 40 per cent. formaldehyde solution and thoroughly mix with a glass rod. Smear the mass over the inner surface of the basin to within 1 inch of the rim with the glass rod, then bake hard on a vigorously boiling steam-bath for 2 hours. Extract the contents of the dish twice with 100 ml of 1 per cent. formaldehyde solution at 40° C; allow 1 hour for each extraction and maintain the temperature at 40° C during the extraction. Filter each washing through a Whatman No. 54 filter-paper and during the final extraction break up the complex and loosen it from the dish. Transfer the complex to the filter-paper and wash it with 100 ml of 1 per cent. formaldehyde solution at 40° C. Determine nitrogen in the complex by the Kjeldahl method. The factor 5·55 is used to calculate gelatin from nitrogen.

Experiments with commercial gelatin show the formaldehyde-precipitable nitrogen to be 95 to 97 per cent. of the soluble nitrogen. Table I shows the recovery of gelatin added to meat extract as determined by five laboratories.

TABLE I

RECOVERY OF GELATIN ADDED TO MEAT EXTRACT

Proportion of added commercial gelatin in mixture, %	Proportion of added gelatin recovered, %				
	A	B	C	D	E
20	127	91	125	110	122
	133	101	127	113	127
	115	113	—	—	—
	—	114	—	—	—
Means ..	125	105	126	112	125
50	116	115	116	103	120
	116	104	116	104	116
	111	94	—	104	—
	—	96	—	—	—
Means ..	114	102	116	104	118

The removal of impurities adsorbed on the gelatin - formaldehyde complex is still under review.

The Determination of Carbonyl Compounds by Semicarbazide and Hydroxylamine

With Special Reference to Fatty-Acid Oxidation Products

BY A. J. FEUELL AND J. H. SKELLON

(*Presented at the meeting of the Society on Wednesday, October 1st, 1952*)

A volumetric method of determining aldehydes and ketones with semicarbazide has been devised. It is suitable for carbonyl compounds that readily precipitate semicarbazones, but it is not applicable to oxidised fatty-acids and esters.

For estimating the carbonyl groups in the products of oxidation of fatty acids and esters by gaseous oxygen, a modified hydroxylamine method is described. The modified method is especially useful for coloured samples.

DURING investigations into the oxidation of monoethenoid fatty acids and esters the need arose for a convenient method of determining carbonyl compounds of the keto- or ketol-acid type, which are known to be formed during these oxidations.[1,2,3,4,5] In an earlier study of an analogous problem, Marks and Morrell[6] concluded that the phenylhydrazine method of Maclean[7] was often unreliable, but the method of Ellis[8] was suitable. Ellis's method involves the use of rather specialised apparatus, which is not always convenient when, as here, carbonyl determinations are required only occasionally and irregularly. For such occasional determinations a straightforward volumetric method seemed to be preferable.

Volumetric methods based on hydroxylamine are in common use,[9] and a selective list of references to the various modifications has been given by Maltby and Primavesi.[10] Nevertheless, it seemed that there would be advantages in devising an alternative method that would permit the isolation of some derivative of the carbonyl compound simultaneously with its quantitative determination, as an aid to characterisation. No volumetric methods based on 2:4-dinitrophenylhydrazine could be traced, although several gravimetric and colorimetric

procedures have been described.[11,12,13,14,15] Of the other common carbonyl reagents, semicarbazide seemed worth investigating, as volumetric methods for its estimation are available.[16,17,18,19,20,21,22] One of the simplest of these methods is that of Smith and Wheat,[22] which involves direct titration with standard iodate. Smith and Wheat identified the carbonyl compounds by finding the equivalent weights of the semicarbazones. For this purpose they prepared the derivative and titrated a weighed amount of it, but did not attempt to determine the percentage of carbonyl group in compounds or unknown mixtures.

Use of semicarbazide

In the first part of our work an attempt was made to extend the method of Smith and Wheat[22] to the direct determination of the carbonyl group in a given material. But an important modification was made in the titration procedure. Smith and Wheat used the iodine monochloride method,[23] but it has been stated[24] that Lang's iodine cyanide method[24,25,26] is preferable for hydrazine and its congeners, although its use for semicarbazide has apparently not been reported. Experiment showed that semicarbazide could be titrated quantitatively and rapidly by Lang's method.

Determination of semicarbazide—

A 0·20 to 0·25-g sample of semicarbazide hydrochloride was dissolved in 25 to 30 ml of water, 20 ml of 5 *N* hydrochloric acid and 5 ml of 10 per cent. potassium cyanide solution were added and the solution was titrated with 0·05 *M* potassium iodate solution. When the solution became light brown (at about 80 per cent. of the complete titre), starch was added and titration was continued until the starch colour disappeared for at least 30 seconds. (1 ml of 0·05 *M* potassium iodate solution ≡ 0·005577 g of semicarbazide hydrochloride.)

As some hydrocyanic acid is evolved during the reaction, it is safer to titrate in a Büchner flask, with the side-arm connected by a flexible tube to a source of gentle suction.

Method for pure carbonyl compounds—

Reagent—Dissolve 3 g of semicarbazide hydrochloride and 3 g of sodium acetate crystals in 100 ml of water. This solution is fairly stable, but a slight loss of strength is unimportant, because a blank determination is always made. The usual titre is about 5 ml of 0·05 *M* iodate per millilitre of reagent.

Procedure—Dissolve 0·2 g of carbonyl compound (for an expected carbonyl content of 20 per cent.; otherwise in proportion) in 10 ml of water or other solvent (see below, p. 137), add exactly 10 ml of reagent and set aside. Filter off the precipitated semicarbazone and

Table I

Effects of time and excess of reagent on formation of semicarbazones

	Salicylaldehyde		Benzaldehyde		
Time allowed for precipitation, minutes	>CO found with E = 1·25, %	>CO found with E = 1·41, %	>CO found with E = 1·21, %	>CO found with E = 1·58, %	>CO found with E = 2·42, %
10	22·1	22·2	25·5	25·6	—
20	22·2	22·2	25·4	25·5	—
30	22·1	22·4	25·4	25·6	24·5
60	22·1	22·4	25·5	25·7	—
>CO calculated, %	..	22·9		26·4	

Note—E is the molar ratio of semicarbazide hydrochloride to aldehyde.

wash the flask and precipitate with two separate 5-ml portions of water, passing the rinsings through the filter and adding them to the filtrate. To the filtrates, whose combined volume is 30 ml, add 5 *N* hydrochloric acid and potassium cyanide, and titrate as above. For the blank, omit the carbonyl compound and dispense with the filtration, but add 10 ml of water before adding the acid and cyanide.

Each millilitre difference between titrations is equivalent to 0·0014 g of >CO. The choice of solvent and the precipitation period are discussed below.

Results—Preliminary tests were made with freshly-distilled salicylaldehyde and benzaldehyde. The first factors studied were the length of time necessary for precipitation and

the effect of excess of reagent. These compounds were always dissolved in 50 per cent. acetic acid and, as an equal volume of aqueous reagent was added, the final acid content of the reaction mixture was about 25 per cent.; the significance of this is mentioned below. The percentage of >CO found is shown in Table I.

It is seen that with these substances useful results can be attained with a precipitation time of only 10 minutes and a 20 to 60 per cent. excess of reagent.

APPLICATION TO KETOHYDROXYSTEARIC ACID—

The method was next applied to a compound typical of those encountered in oxidation researches, namely, ketohydroxystearic acid. A pure specimen was prepared by King's method,[1] but the 9:10 and 10:9-isomers were not separated, as this was unnecessary for the purpose in hand. The purity of the specimen, found by titrating an alcoholic solution with standard alkali, was 99·2 per cent., corresponding to a carbonyl content of 8·84 per cent. (calculated, 8·91 per cent.). King[1] showed that the semicarbazone of this acid could be precipitated from 60 per cent. alcohol, and these conditions were used for the determination.

Procedure—Dissolve 0·4 g of the ketol acid in 16 ml of alcohol and add 10 ml of reagent. Precipitation of the semicarbazone begins within about half-an-hour and is completed overnight. Filter, rinse, and titrate the filtrate as previously described; make a blank determination simultaneously.

Three separate determinations gave 8·75, 9·06 and 8·87 per cent. for the carbonyl content.

EFFECTS OF SOLVENT AND TEMPERATURE ON STABILITY OF SEMICARBAZIDE SOLUTIONS—

Trials were made to determine the effect of temperature, as it seemed likely that it might occasionally be desirable to precipitate at other than room temperature. Erratic results under certain conditions were traced to unequal changes in titre between sample and blank, owing to decomposition of the semicarbazide. These changes were investigated systematically by setting aside blanks containing a fixed amount of the semicarbazide reagent in water or in one of three different strengths of acetic acid or alcohol for various times at three widely different temperatures. The results in Table II show the differences between initial and final titrations for pairs of similar blanks. It must be remembered that in practice decomposition will occur in both sample and blank; if these changes are equal there will be no error, but, owing to differences in concentration arising from the removal of semicarbazide in the precipitate, the amounts of decomposition will not generally be identical. The titration errors will, however, be less than the differences shown in Table II, which can be regarded as the maximum.

TABLE II

EFFECTS OF TIME AND TEMPERATURE ON DECOMPOSITION OF SEMICARBAZIDE IN DIFFERENT SOLVENTS

Solvent	Concentration of solvent, % v/v	Titre differences after setting aside at: 0° C for 8 hours, ml	16° C for 2 hours, ml	16° C for 4 hours, ml	16° C for 8 hours, ml	45° C for 2 hours, ml	45° C for 4 hours, ml	45° C for 8 hours, ml
Water ..	100	0·05	0·00	0·10	0·15	0·05	0·15	0·15
Acetic acid ..	75	0·45	0·30	1·10	1·75	7·35	12·55	—
	50	0·15	0·30	0·85	1·60	5·90	10·40	—
	25	0·05	0·20	0·25	0·60	2·85	6·25	—
Alcohol ..	75	0·50	0·55	0·50	0·55	1·15	1·25	2·15
	50	0·35	0·25	0·30	0·40	0·90	0·75	1·05
	25	0·05	0·10	0·15	0·20	0·40	0·30	0·40

It is clear that prolonged heating is undesirable when acetic acid is used as the solvent; but, in determinations made as above, in which the final concentration of acid in blank and sample solutions is about 25 per cent. and the procedure is completed in 30 minutes or less, decomposition causes only a slight error. Water or dilute alcohol can be safely used for fairly long precipitation periods at room temperature, and at low temperatures any of the solvent mixtures appears to be suitable.

APPLICATION TO OXIDISED MATERIALS—

Monoethenoid fatty-acids and esters, after catalytic autoxidation for several hours at temperatures above 100° C, develop reducing properties, which are apparently due to the formation of various types of carbonyl compounds.[2,3] The application of the semicarbazide method to oxidised oils possessing marked reducing properties was disappointing, as semicarbazones could not be precipitated; the method consequently failed. It was difficult to find a suitable solvent; the oxidised products are not soluble in 50 per cent. acetic acid, and, in view of the results shown above, a solution of any greater strength could not be used. Although soluble in 95 per cent. alcohol, the oils are precipitated as soon as the added water reduces the alcohol content to less than about 85 per cent.; hence the 60 per cent. alcohol conditions suitable for a pure ketol acid are inapplicable. Pyridine, which Hopper[27] showed to be a useful solvent for preparing semicarbazones, proved unsuccessful. Moreover, its basicity caused a further complication, which would have made its use doubtful in any event; for although additional concentrated hydrochloric acid was added before titration, a buffering effect seemed to retard the iodate reaction, and the end-point, which showed considerable drift, was reached slowly. Immiscible solvents such as chloroform were also investigated, but, even after shaking and setting aside for long periods, semicarbazones were not precipitated.

USE OF HYDROXYLAMINE

In view of the inapplicability of the semicarbazide method to oxidised materials it was decided to use hydroxylamine, and the recent method of Maltby and Primavesi[10] was selected. Careful matching of the bromophenol blue indicator at the end-point is essential in this method, but it was at once found that the procedure as published was not reliable for oxidised fatty compounds, since these were generally reddish-yellow or brown; they changed the tint of the indicator so much that it could not be properly matched against the standard. In addition, matching was found to be rather difficult in artificial light. As a result of further work, Maltby and Primavesi's method was modified in two ways, as follows—

(1) By the use of two reagent solutions instead of a single one, so that interference from colour inherent in the sample is eliminated and, to a lesser extent, variations from neutrality in the sample are simultaneously compensated. Both these improvements can be achieved by using only about 25 per cent. (by weight) more of sample than is required for a determination by the original method.

(2) By making the matching procedure equally easy in either daylight or artificial light.

The method devised is as follows.

METHOD—

Hydroxylamine reagents—Reagent A. Dissolve 20 g of hydroxylamine hydrochloride in 100 ml of water, make up to 1 litre with 95 per cent. alcohol, and add 25 ml of a 0·2 per cent. alcoholic solution of bromophenol blue. Heat on a water-bath for 30 minutes to react with any carbonyl compounds in the alcohol, cool, and adjust the colour as seen in the bulk to the neutral dichroic green-red with 2 *N* alkali.

Reagent B. Prepare as for reagent A but use 5 g of sodium or ammonium acetate instead of the hydroxylamine; this imparts a slight buffering action. This solution need not be heated. Adjust its colour with 2 *N* acid until it matches that of reagent A. The exact tint is not critical within reasonable limits, and it is immaterial whether reagent B is adjusted to match reagent A or *vice versa*. The solutions keep well, but should be re-matched before they are used. Prepare 4 volumes of reagent A for each volume of reagent B.

Matching—Match in paired boiling or Nessler tubes instead of in conical flasks as in the original method, using about 20 ml of each solution. Hold the tubes vertically side-by-side and view horizontally against a piece of opal glass illuminated from behind by a fairly strong light. This technique is both convenient and accurate. In the small thickness of liquid viewed, the indicator colour is a distinct green in contrast to the dichroic green-red displayed by a larger bulk in a flask, and slight differences in tint are more easily perceptible. By day, reflected sunlight from walls or a strong north light are equally suitable for illuminating the opal glass screen, whilst at other times a 60, 75 or 100-watt bulb placed about a foot behind the screen is adequate. Moreover, slightly turbid solutions, which are difficult to compare,

even in tubes, against ordinary backgrounds, can be matched against the opal screen, the turbidity apparently disappearing.

Procedure—Dissolve the sample (corresponding to 0·002 to 0·004 gram-molecules of carbonyl compound) in 25 ml of water or alcohol, and add 20 ml of this solution to a flask containing 60 ml of reagent A. Add the remaining 5 ml to 15 ml of reagent B in one of a pair of tubes. The colour of the indicator in both reagents is thus equally affected by dilution and inherent sample colour.

Set the sample aside for 5 to 10 minutes and then titrate it with 0·2 *N* alkali to match reagent B, a proportionate amount of water (one-quarter of the titration volume) being added to reagent B. With a little practice it is possible to titrate the liquid in the flask to a point just on the acid side of neutrality, as seen by the colour in bulk. Pour some of the mixture into the other tube and compare the two as described. If the liquids are not matched return the contents of the tube to the flask and cautiously continue to titrate, transferring a suitable volume to the tube from time to time for exact comparison. When the solutions are matched,

TABLE III

RESULTS BY PROPOSED METHOD APPLIED TO OXIDISED MONOETHENOID ESTERS

Sample	>CO found at 55° C, %	85° C, %	120° C, %
Oxidation products of ethyl oleate	0·64	1·86	1·95
" *n*-propyl oleate ..	0·78	1·91	1·88
" *n*-butyl oleate ..	1·09	1·99	1·83

set them aside for a further 5 to 10 minutes and compare them again, as some compounds react slowly. Finally, loosely stopper the two flasks, place them on a water-bath for 20 minutes, cool and titrate if necessary to ensure final matching; this may be necessary for compounds that do not react in the cold. Water must always be added to reagent B in the same proportion, one-quarter of the titration volume, before final matching.

A slight departure from neutrality, such as is given by many organic acid samples, causes no serious interference. Strongly acid or alkaline samples are dissolved in water or alcohol, a drop of bromophenol blue solution is added and the colour adjusted approximately to the neutral tint with alkali or acid. The volume is then made up to 25 ml and the procedure carried out as described above.

An improvement in technique,[28] which allows more rapid manipulation, is effected by titrating the sample in a standard-joint flask having a long narrow neck equal in diameter to the tube containing reagent B. For matching, a stopper is inserted, the flask inverted, and the columns of liquid in the neck and tube are compared as usual.

Results—Since hydroxylamine is well established for estimating the commoner aldehydes and ketones, trials with the modified method were mainly concerned with the effects of colour in the sample. Satisfactory results were obtained with salicylaldehyde and anisaldehyde each tinted with brown dye; mean percentages of >CO group found were, respectively, 22·7 and 20·1 per cent. (calculated, 22·9 and 20·6 per cent.). Ketohydroxystearic acid, mixed with various amounts of brown dye in imitation of the oxidation products for which the method was ultimately to be used, was then tried. Even with highly coloured samples there were no difficulties with the modified method. The carbonyl content found in a series of runs with 0·5 to 0·6 g varied from 8·88 to 9·13 per cent. (calculated, 8·91 per cent.). An even more representative test was made by dissolving some of the ketol acid in oleic acid and again adding brown dye, thus closely simulating a possible oxidation product. The mixture contained 15·4 per cent. w/w of ketol acid (equivalent to 1·37 per cent. of >CO). Three separate determinations indicated 1·42 to 1·45 per cent. of >CO, which corresponded to 15·9 to 16·3 per cent. w/w of ketol acid.

Application of the method to oxidised monoethenoid esters has enabled the influence of temperature and constitution on formation of carbonyl groups to be studied. Some typical results are indicated in Table III, which shows the percentage of >CO found in three homologous esters autoxidised at different temperatures in presence of a uranium catalyst.

Subsequent work on oxidised materials has shown that the method can be scaled down if necessary and applied to smaller samples with the use of 0·1 *N* alkali, a match to within

one drop still being readily attainable. Occasionally it is desirable to titrate with alcoholic alkali, as certain complex products, such as those from oxidised butyl oleate, are precipitated if appreciable amounts of aqueous alkali are added; a proportionate volume of alcohol instead of water is then added to reagent B before matching.

The method has been found useful for studies of the carbonyl content of the various fractions obtained in the separation of the complex end-products of oxidised fatty-acid esters (being prepared for publication elsewhere). It has also been used to follow the steady decrease in carbonyl content occurring during the thermal catalytic autoxidation of ketohydroxystearic acid.[28]

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August 22nd, 1952

A Brief Survey of the Development of Electrographic Analysis

With Special Reference to Recent British Apparatus

By P. R. MONK

(*Presented at the meeting of the Physical Methods Group on Tuesday, February 19th, 1952*)

A brief account is given of the development of electrographic analysis, from the time of its origination by Glazunov and Fritz in 1929 up to the present day. The technique is described, and details are given of recent British apparatus of two types, including several examples of their use.

In 1906, Baumann[1] devised a method of showing sulphide inclusions in steels by placing the polished specimen in close contact with ordinary photographic paper soaked in dilute sulphuric acid. The silver salts in the emulsion were blackened by sulphides, and not only was the presence of sulphide demonstrated, but a print showing the shape and location of the inclusions was produced. Since then, this method, and others for spot-testing metals,[2] have been applied widely, but all suffer in consequence of the strongly acidic media required for dissolving the metals. These acids are not only unpleasant to handle, but often preclude the use of certain sensitive reagents.

In 1929, this trouble was overcome by Glazunov[3] and Fritz,[4] working independently and with different aims. Their solution to the problem was simple and effective. In place of strong acids, they used electrolytic attack with neutral salt solutions. With the sample as anode, the solution was held in porous paper, and another metal, which did not participate in the reaction, was made the cathode.

Glazunov applied the technique to give metallographic prints, and Fritz worked on spot tests for identification purposes. Little further work was published until the beginning of the war, when Hermance[5] gave details of the practical use of the method, both for identifying metals and for checking plated coatings, such as those on telephone contacts, for wear. He described methods for chromium, nickel, lead, tin, copper and zinc, but did not describe his apparatus in detail.

Shortly afterwards, in 1941, Calamari[6] developed a method for chromium in steels. With a graphite rod as counter-electrode, he applied 9 volts from six large dry cells. Then Hunter, Churchill and Mears[7] made a wide survey, covering a large number of metals, and suggested the use of a block of eighteen metals as a "standard." Their counter-electrode was aluminium.

In 1943, Calamari, Hubata and Roth[8] described a method for molybdenum in steel, which utilised the equipment they had described earlier.[5]

From this time onwards publications were fairly frequent,[9,10,11] and in 1949, Hermance and Wadlow presented a comprehensive paper at a Symposium on Rapid Methods for the Identification of Metals before the American Society for Testing Materials.[12]

But without the pioneer work of Fritz Feigl,[13,14] who developed the use of filter-paper for spot tests, it is doubtful whether the modern electrographic method would have developed so far. His discovery that the use of filter-paper increases the sensitivity of many spot tests has been invaluable and the method includes many of the tests he has devised.

Modern electrographic method—

The method depends mainly on electrolytic solution. The test sample is made anode in a small cell, and the electrolyte, which soon contains some of the metal in solution, is "developed," *i.e.*, treated with a reagent to give a characteristic colour. Instead of working in "bulk" solution, the electrolyte is absorbed in filter-paper, Whatman No. 3 filter-paper being suitable for spot-testing. This paper is placed between the sample and a counter-electrode or cathode, generally made of aluminium. Current is passed for a short time (10 to 15 seconds), and finally appropriate reagents are added. The whole test can often be completed in 1 minute or less.

Generally, a simple salt solution, *e.g.*, sodium nitrate or ammonium chloride solution, which plays no part in the subsequent development, is used as electrolyte. But occasionally it is of great help to use as the electrolyte a salt that will form a colourless complex with an interfering metal. Sodium fluoride is used in this way to suppress the effect of iron in certain tests.

The developers used are frequently the new organic reagents,[15,16,17] but in some tests these do not work sufficiently well under the working conditions and the older inorganic tests are applied.

The sensitivity of the tests is high, often only a microgram or less of the metal being required. This is one of the advantages of the method, as little damage is caused to the

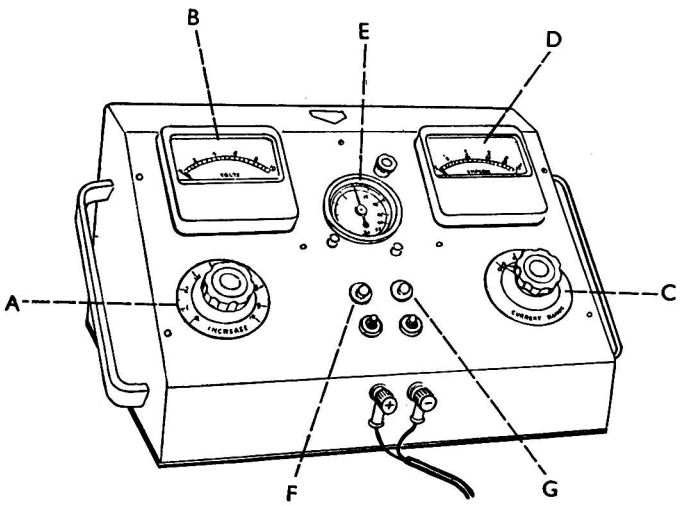

Fig. 1. Power supply unit of spot-test apparatus (laboratory model)

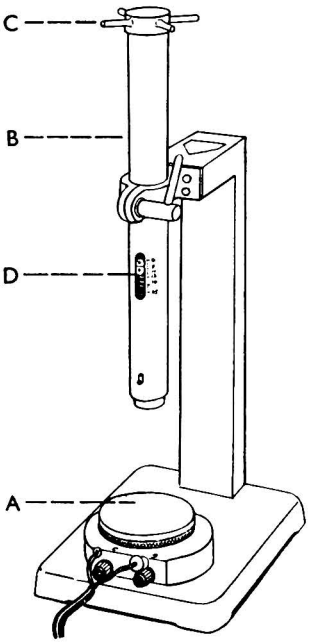

Fig. 2. Sample holder (laboratory model)

specimens beyond a slight staining. Hence the composition of finished parts can be checked without destruction. There are also several other applications: metallic inclusions can be identified readily and quickly, metallographs can be prepared, which show the distribution of alloy ingredients, and it is an excellent and sensitive method for detecting pinholes in the coatings of painted and plated parts.

APPARATUS—

The basic requirements are simple; a source of low-voltage direct current, and various electrodes, but for consistent working, or for "standardised" tests on coatings, more elaborate and better controlled equipment is needed.

Fig. 1 shows recent apparatus designed specifically for this type of work. The "Laboratory Model" is A.C.-mains powered, as dry batteries were considered unsatisfactory for this purpose. The output can be varied continuously from 0 to 10 volts by control A, at up to 5 amperes in three ranges. Meters are fitted; the voltmeter, B, indicates the potential difference across the sample - paper - counter-electrode combination, and the range switch, C, on the ammeter, D, also sets the maximum current available in each range.

This switching arrangement prevents damage to the instrument should the paper be pierced accidentally; a short circuit can be maintained indefinitely without harm.

As the length of time during which current is passed is important when methods are standardised, a process timer, E, is fitted. This eliminates the human error associated with

stop-clocks, and enables the operator to prepare the next specimen while the first is being tested. The timer is variable up to 60 seconds, and is re-set automatically.

Two pilot lights are fitted, F indicating "Power on, timer motor running" and G "Output on."

The sample holder (Fig. 2) is separate, being connected to the power supply unit by a flexible cable. The base carries the aluminium counter-electrode, A. This is detachable and although this is normally a flat plate, it can be easily replaced by specially shaped electrodes when required. Placed centrally above this is a pressure-bar, B, which applies a known load and makes electrical contact with the sample. The load can be varied up to 25 lb by rotating the hand-wheel, C, at the top. The thrust is shown on the small scale, D, in the lower part of the bar.

An apparatus of this kind is not always convenient or necessary, especially when spot tests only are required, as in metal stores and scrap yards, and Fig. 3 shows a special "Pocket Model" for these purposes. It does not incorporate all the controls of the "Laboratory Model," but is nevertheless efficient for detecting a wide range of metals.

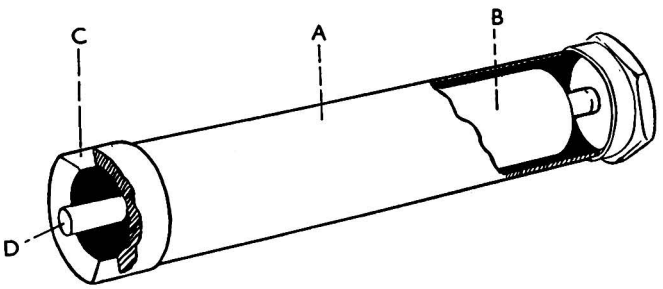

Fig. 3 Spot-test apparatus (pocket model)

The body, A, carries two standard pocket lamp cells, B, so fitted that the case is made positive. This is connected to the sample via the slotted contact ring, C, at the end. The counter-electrode is a centrally fitted aluminium plunger, D, which is spring loaded, and connects to the negative pole of the battery via a simple switch.

Operation is simple. A small circle or strip of filter-paper damped with the appropriate electrolyte is put on the sample, and the plunger is placed against it. With care being taken that the contact ring does not touch the paper, the apparatus is pushed home firmly, so that the contact ring connects to the sample. The pressure is maintained for 10 to 15 seconds, then the paper is removed and treated with the appropriate developer.

PRACTICAL APPLICATION OF THE METHOD—

Both models are suitable for spot-testing metals in order to check or discover their identity. For example, a stainless steel may be specified as containing molybdenum, but some doubt may have arisen as to whether in fact it does. A rapid test can be carried out as follows.

Rapid procedure—Use either 5 per cent. hydrochloric acid or 5 per cent. ammonium chloride solution as electrolyte. Pass current at about 3 volts for 10 to 15 seconds, and develop the stain by adding 1 drop of 1 per cent. ammonium thiocyanate solution. Allow the paper to soak for about 1 minute in 1 per cent. stannous chloride solution dissolved in 5 *N* hydrochloric acid. A brick-red stain, remaining after the disappearance of the deep red ferric thiocyanate colour confirms the presence of molybdenum.

Alternatively, it may be necessary to distinguish between zinc and cadmium plating. With 10 per cent. sodium nitrate solution as electrolyte and 10 per cent. sodium sulphide solution as developer, cadmium gives a vivid yellow colour and zinc no colour.

The presence of cobalt in tool and magnet steel can be shown by using 5 per cent. sodium fluoride solution as electrolyte and a saturated solution of potassium thiocyanate in acetone as developer. A vivid blue-green colour indicates cobalt. This is an example of the use of a complexing electrolyte; the sodium fluoride prevents interference from iron.

In all, rapid and economical methods such as these have been worked out for sixteen metals.

Metallic inclusions in metals are best detected by means of the "Laboratory Model," which gives a print showing not only the presence of any inclusion, but also its shape, size and position. For this work a paper coated with hardened gelatin is better than filter-paper, which is coarser grained. Both Glazunov[2] and Hermance[7,12] have had success with these methods.

For example, trouble may have been experienced with suspected iron inclusions in an aluminium alloy. With ammonium chloride as electrolyte and potassium ferrocyanide as developer the presence of the inclusions can be confirmed.

The procedure is also useful for the detection of pinholes in painted and plated finishes. Again the "Laboratory Model" should be used, but reagents should be chosen to detect the underlay or base metal. For example, porosity in chromium plated over nickel can be checked with sodium fluoride as the electrolyte, and pinholes can be shown by the red nickel colour given with dimethylglyoxime or "Nioxime." Pinholes in paint applied over iron can be detected with the ferrocyanide method mentioned above.

APPLICABILITY OF THE METHOD—

Electrographic technique is rapid and useful for spot-testing metals and alloys, and for detecting and delineating imperfections in both solid metals and coatings. No strongly corrosive acids are required, and damage to the sample is negligible. Apparatus has been developed both for simple spot-testing and for more detailed metallographic work. Methods are available for a wide range of metals and alloys, and the technique should be of great value to all those who use and test metals.

I thank the Directors of Baird & Tatlock (London) Ltd., for their permission to publish this paper.

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The Identification of Alloys and Stainless Steels by Electrographic Methods

By G. C. CLARK and E. E. HALE

(*Presented at the meeting of the Physical Methods Group on Tuesday, February 19th, 1952*)

A method is described for the identification of certain stainless steels and other alloys used in the construction of chemical plant. An electrographic method, which obviates drilling or cutting, is used for testing the sample.

The constituents shown on the electrogram are identified by a series of spot tests applied systematically to classify the type of material from which the plant is made.

The method is simple, the apparatus is portable and can be used on any site.

Copper and nickel alloys and stainless steels are becoming increasingly important in the construction of chemical plant. The presence of certain "stabilising elements" in the stainless steels has a considerable effect on their resistance to corrosion.

If the construction of new plant is to be considered, it is possible to test known specimens before a decision is made as to their suitability. However, when it is necessary to check the performance of existing plant or to purchase second-hand plant or job lots of sections or plate the question of identity arises.

As records are frequently unreliable or even unobtainable, recourse has to be had to some analytical procedure that will supply the information.

A fully equipped metallurgical laboratory would be able, eventually, to identify a specimen, which would have to be obtained by drilling or cutting, but this method could obviously not be used for existing plant or plant offered for sale. The time that elapses before the full result becomes known may be too long in a second-hand plant sale.

A simple method of identifying plant and plant materials is set out here, which althougn it has only been applied to a limited range of alloys, is amenable to elaboration.

The sample is taken, by means of an electrogram, on filter-paper moistened with a neutral electrolyte.[1,2] An electrolytic solution of the test material is produced by connecting the positive pole of a source of continuous current to the test material and by completing the circuit through the moist paper to an electrode connected to the negative pole. The ions are quickly driven into the paper, where they can be identified by a series of spot tests.[3,4,5]

Method

Apparatus—

A source of continuous current is required, which can be two or three dry cells in series. A cycle-lamp battery will give 3 volts or the slightly larger rectangular battery will give 4½ volts and provide the electrogram in a shorter time.

Filter-paper pads should be made by folding strips of Postlip 633A, Whatman No. 1, or other similar grade of filter-paper, 1 inch wide by 5 inches long, six times to make pads approximately 1 inch long by ¾ inch wide.

Two electrodes of copper or aluminium are also needed. The electrodes can be conveniently made from 16-gauge copper or aluminium sheet about 2 inches square. One piece is bent at a right angle, about ¾ inch from one edge, to form a finger grip. Single leads of flexible wire about 1 yard long are attached to each electrode. When testing a piece of plant a third electrode is useful. This can be a piece of brass rod about ¼ inch in diameter, or the central carbon rod from an exhausted dry battery.

Reagents—

A *N* solution of potassium chloride and bottles of reagents provided with capillary dropping pipettes for the spot tests.

PROCEDURE—

To prepare a suitable site for the test on the plant or specimen, remove adherent dirt, scale or paint by scraping an area of about 1 square inch. This site can be on the rim outside or inside of a vessel, as is most convenient. The inside can be used if a vessel is constructed from mild steel clad with an alloy. Avoid highly polished surfaces, as mirror polishes will be dulled by the electrolysis.

Connect the electrodes to the battery, with the bent electrode to the negative pole. Moisten a pad of the filter-paper with 4 or 5 drops of *N* potassium chloride solution, avoiding any excess, and place it on the cleaned area of the specimen. Hold the pad firmly in place by exerting firm pressure with the bent, that is, negative, electrode. Hold the positive electrode on the specimen, adjacent to, but not touching, the moistened paper pad. This completes the circuit and generally produces a suitable electrogram after about 1 minute.

To identify the metals add drops of spot-test reagents from a capillary dropper to portions of the electrogram. It is important that no excesses of reagents be used or the paper will become flooded. Unfold the paper pad and cut off the portion of the strip that has been in contact with the specimen. Cut this strip, which is usually coloured, into six narrow strips.

Apply the tests in the following way, but modify the scheme as necessary to suit any specific requirements.

1. Hold one of the strips in ammonia vapour—

A bright blue colour indicates copper.
A paler mauvish colour indicates nickel.
A brown or dirty-green colour indicates iron.
A greyish colour indicates iron plus copper or nickel.

Copper is confirmed by spotting the strip with sodium di-ethyldithiocarbamate; a brown stain develops.

Nickel is confirmed by spotting the strip with dimethylglyoxime solution, which gives a red colour.

Iron is confirmed by spotting a fresh strip, which has not been held in ammonia vapour, with potassium ferrocyanide; a blue colour develops.

Nickel in the presence of iron is confirmed by adding a drop of tartaric acid solution to a fresh strip and then adding a drop of dimethylglyoxime solution. On holding the strip in ammonia vapour a red colour develops.

Copper in the presence of iron is confirmed by the same procedure except that sodium di-ethyldithiocarbamate is used in the place of dimethylglyoxime.

2. Apply a spot of potassium thiocyanate solution to another strip. A red-brown colour indicates iron. Apply stannous chloride to the red-brown stain. If this colour is discharged and a carmine colour develops, molybdenum is present.

3. Apply stannous chloride to a fresh strip and then add a spot of chromotropic acid solution. A reddish-brown colour indicates titanium. The minimum amount of stannous chloride should be used as it reduces the sensitivity of the test. As most chromotropic acid solutions are brown, it is advisable to place some on a piece of filter-paper and to compare this with the strip of the electrogram used for the testing for titanium.

4. Apply a drop of diphenylcarbazide solution to the remaining strip. A violet colour indicates chromium.

Iron, nickel, chromium and molybdenum indicate a stainless steel stabilised with molybdenum.

Iron, nickel, chromium and titanium indicate a stainless steel stabilised with titanium.

Nickel and copper indicate Monel or a similar alloy.

Iron, nickel and chromium indicate Inconel or an ordinary stainless steel.

It will be noted that one electrolyte, potassium chloride, has been used for all these tests. This is not necessarily the best solution for all specimens and if the method is to be used for regular routine work, solutions of other salts may give better results with certain elements. As an example, with certain of the stainless steels a better test for chromium is given when potassium nitrate is used as the electrolyte, and for copper alloys sodium sulphate solution gives slightly better results.

So far the test has only been used qualitatively, and the following suggestion is offered and may lead, if not to a strictly quantitative test, at least to a comparative test that might

be of value in distinguishing between the austenitic 18 - 8 stainless steels and the low chromium - nickel steels that are also used for chemical plant.

It is quite possible that paper chromatography would separate inorganic elements[6,7,8,9] from the electrogram. The resulting chromatogram when developed with appropriate reagents would give coloured areas proportional to the quantity of the elements present and so the amount of the elements present in the original specimen could be assessed. A certain amount of success along these lines has been achieved, but further work is needed before the method can be established.

The authors express their thanks to the Directors of Howards and Sons, Ltd., of Ilford, Essex, for their permission to publish the results of this work, which was carried out in the Works Analytical Department.

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March 4th, 1952

Discussion on the foregoing two papers

Mr. A. A. Smales asked if either author had yet been able to identify stainless steels containing up to 1 per cent. of niobium or tungsten and whether it was possible to say with certainty whether a steel contained more than a specification minimum, when this minimum was about 0·5 per cent. of the elements titanium, niobium and tungsten. He also asked if the electrographic technique had proved of value in the identification of minerals.

Mr. Monk said that neither he nor Mr. Hale could offer a suitable chemical spot test for niobium. He had conducted experiments with tungsten, for which the Rhodamine B test might be suitable, without success.

In reply to Mr. Smales' second question, he said that, provided suitable tests were available, comparison under controlled conditions with standard samples should give a reasonable estimate of the amounts present.

Mr. Hale said that it was doubtful whether an assessment of the quantity of alloying metal could be made by the method described in their paper. If a rigorously standardised procedure were adopted, *i.e.*, if the time of electrolysis, pressure of electrode, current density, thickness of paper, and so on, were made the same, then by comparing electrograms from standard samples of known composition with the electrograms of the test sample a semi-quantitative result could be obtained.

To Mr. Smales' third question he said that the electrographic identification of minerals described by R. Jirkovsky (*Chem. Listy*, 1931, **25**, 254; *Chem. Abstr.*, 1931, **25**, 5640) was one of the early applications of electrographic analysis. The mineral must be a conductor of electricity.

Mr. D. G. Higgs said that he had been much impressed by what he had seen at the meeting. His own experience of electrographic analysis had been fairly limited; he had abandoned the procedure early in the forties, as it was too restricted for his purposes, *viz.*, spot testing. It was interesting to hear that Mr. Hale had also been unable to find a suitable spot-test reaction for niobium in stainless steel, it being one of the three elements that had completely outwitted him in his own researches.

With regard to the other metals used as stabilisers in the 18 - 8 type of steel, he had reliable tests for titanium, tungsten and molybdenum, but not for tantalum, which was often used as a substitute for niobium. He asked Mr. Hale whether the technique he had described could detect as little as 0·1 to 0·3 per cent. of titanium easily, since if molybdenum was also present the amount of titanium needed to convert all the carbon to carbide could be considerably reduced below the amount already indicated, namely, 1 per cent.

Mr. Higgs drew Mr. Smales' attention to a paper, which included good multicolour electrographs of various metallic minerals (Gutzeit, G., American Institute of Mining and Metallurgical Engineering, Technical Publication No. 1457, March, 1942).

He had always maintained that it was impossible to interpret spot-tests quantitatively, there being so many variables that could not readily be controlled. The apparatus shown by Mr. Monk might go a long way towards achieving this end; would the author say something about his experience in this connection.

MR. MONK agreed that quantitative interpretation of the results should be made with caution, but by rigidly controlling conditions, as with the "laboratory model," results should be reasonably accurate. Comparison should be made with known samples of similar type.

He said, on the second point, that he had had little personal experience, as he had been concerned mainly with the development of the apparatus. Mr. Higgs might like to see an account of the work of Glazunov and his associates (*Chem. Zentr.*, 1941, **II**, 2865; *Korrusion u. Metallschutz*, 1946, **16**, 341).

MR. HALE said that the electrographic method should detect as little as 0·1 to 0·3 per cent. of titanium, if care was used in applying the spot-tests. The chromotropic acid solution should be freshly prepared, and the minimum quantity of stannous chloride solution, preferably diluted, used to suppress the iron colour.

MR. H. STANT asked why pressure was varied between electrodes and why aluminium was made cathodic. He asked if it was possible to detect iron, copper, manganese and cobalt in pure nickel and whether it was possible to distinguish between residual elements, low alloy elements and highly alloyed materials.

MR. MONK said that pressure was made variable so that the optimum conditions might be chosen and allowance could be made for different sample areas.

In anodic dissolution (the opposite of electroplating) the sample was the anode and, hence, the aluminium, which acted only as the second electrode to complete the circuit, was the cathode. Other metals could be used, platinum was ideal, but aluminium was generally suitable.

Iron, copper and cobalt should be fairly easy and manganese somewhat more difficult, but all tests depended on the actual proportions present, which might be below the sensitivity limit. It should be remembered that the total sample taken was only a few micrograms.

In reply to the last question, he said that distinction depended on amounts present and on the sensitivities of the tests for the metal concerned. In general, highly alloyed materials would give a strong colour, low alloy elements a weak but definite colour, and residual elements weak or indefinite results.

Replacement of Standard Cell and Salt Bridge by Indicator Electrodes and the Use of Non-Aqueous Solutions in Potentiometry

Part II. Iodometry and Iodimetry in Aqueous Solution

By E. BISHOP*

The use of reference indicator electrodes in the titration solution to replace the standard reference cell and salt bridge in potentiometric analysis has been extended to electron transfer reactions, and indicator electrodes responsive to ion combination reactions have been applied to redox reactions involving the iodine - iodide system. The glass reference indicator electrode, in solutions not too strongly acid, has been found admirable in all three types of procedure and gives unexceptionable results. The silver reference indicator electrode is eminently suited to procedures involving the titration of reducing agents with standard iodine, and to titration of iodine, either standard or liberated by an oxidant from an excess of iodide, with standard reductants. In procedures involving direct titration of an iodide with an oxidant, its behaviour is not that of a constant potential electrode, but depends on the normal potential of the oxidant. The behaviour of the antimony reference indicator electrode is complicated by its existence in alternative valency states; however, the electrode gives excellent results in all three types of procedure. It is shown that accuracy with reference indicator electrodes equals that of the accepted technique, with a standard calomel half-cell and salt bridge, and that qualitatively (equilibration speed and sensitivity of measurement with low impedance potentiometers) some advantage, in addition to simplicity, over the classical method is offered.

The titration cell used in potentiometric analysis consists of an indicator electrode, whose potential varies with the concentration of a reacting ion, in combination with a reference electrode, whose potential remains constant during the determination. Usually the second electrode is a standard half-cell, such as the saturated calomel electrode, electrically connected by means of a salt bridge to the titration solution containing the indicator electrode. In titration work, the reference electrode should furnish a steady potential, unaffected by the nature of the reaction being studied, and one to which the varying potential of the indicator electrode can be referred. An indicator electrode in a solution stabilised or buffered with respect to the indicated ion will furnish the required steady potential, and there is no reason why such a "reference-indicator" electrode should not be placed in the titration solution itself, provided there is no interaction between the system of ions maintaining the reference indicator potential and the reagents whose reaction is being followed by the "reaction indicator" electrode. Bishop[1] applied this principle in the use of pH indicating reference electrodes in precipitation reactions, when glass and antimony gave excellent results in argentometric determinations of halides and thiocyanate in aqueous media containing free nitric acid, and also in non-aqueous amphiprotic media stabilised with ammonium salts. The poising of the solution with respect to the reference indicator ion was not critical. The application of a redox reference indicator electrode to these reactions did not give a constant reference potential, but gave accurate results of diminished sensitivity in unpoised solutions; in redox systems poising gave rise to unexplained anomalies.

Experimental

This paper begins an examination of the application of "ion combination reference indicator" electrodes to electron transfer reactions. Certain electrodes function in more than one way; for instance, antimony, arsenic, hydrogen and quinhydrone are used as pH indicating electrodes, but depend upon or are affected by oxidation reactions, and mercury

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as a pHg indicating electrode is influenced by oxidation; this makes them inapplicable to electron transfer reactions as reference indicator electrodes, unless the effect can be overcome and a valency state fixed and retained. An ideal reference electrode should neither influence (electrically) or contaminate (chemically) the titration solution, nor be influenced or contaminated by the titration solution. Within the pH limits set by the acid and alkali errors, the glass electrode fulfils this condition admirably, and it was from this realisation and its application in cerate oxidimetry some years ago, that the reference indicator electrode principle[1] originated and the present work developed.

Previous applications of the glass electrode to titration work have been made by Lykken and Tuemmler[2] and have been embodied in standard analytical methods in the petroleum industry.[3] Bates[4] has used the same principle to eliminate liquid junctions in the precise determination of ionisation constants by titration, for which the potential of the reference electrode had to be both accurately known and perfectly steady, by a combination of a silver - silver chloride electrode in solutions of uniform ionic strength with a hydrogen reaction indicator electrode.

A great number of useful procedures are based on the iodide - iodine redox system[5] and these can be classified into three groups as follows—

(1) Direct titration of iodide by an oxidising agent to give free iodine.

(2) Direct titration of reducing agents by means of standard iodine solutions.

(3) Titration of free iodine, either as a standard solution, or liberated from an excess of iodide by an oxidant, by means of a standard reductant, such as thiosulphate or arsenite.

For the second and third of these groups the end-point is normally indicated by starch, which is both convenient and accurate. Reactions of the first group require electrical methods for locating the end-point, or an indirect back-titration method, inherently of lower accuracy, and it is with this group that the principal advantage of the potentiometric approach lies. In the first group, loss of iodine by volatilisation, instead of being a source of error carefully to be avoided, is often advantageous. Furthermore, it is often possible to work in an acidity range in which direct or induced air oxidation of iodide is minimised. A possible disadvantage lies in oxidation of iodine to iodate; the acidity and salt concentration of the solution are insufficient to support formation of I^- ions. This can often be overcome by controlling acidity and removing the liberated iodine by a solvent and, although it may reduce the size of the potential break at the end-point, it does not necessarily cause errors, since consumption of oxidant by this reaction does not occur until the end-point has been passed.

Although less popular for reactions in groups 2 and 3, the end-point curves for the potentiometric method are particularly steep, and the enhanced precision of end-point location thereby offered, coupled with the ease and speed of operation, compensate for the additional complication in technique. Errors due to volatilisation of iodine can be overcome in suitable apparatus, and the methods now proposed eliminate the disadvantage of increased internal electrode resistance and sluggish potentiometer response on the low-potential side of the end-point, which may give rise to uncertainties of 50 mV or more with standard low resistance potentiometers and the calomel cell and salt bridge. To provide for this second possibility, titrations of iodine, standard or liberated, by thiosulphate, arsenite or antimonite are preferred to titrations of reductants by standard iodine delivered from the burette.

Ion-combination indicator electrodes include pH electrodes (glass, antimony, arsenic, and so on), precipitation electrodes (silver), complexation electrodes (silver) and association electrodes (mercury). Provided there is no chemical interaction between reference indicator and reaction indicator systems, any of these electrodes can theoretically be used for reference purposes in electron transfer reactions. Glass, antimony and silver electrodes have been successfully applied to various titrations involving iodine.

In all reactions, the glass electrode acts perfectly as a constant potential generator, and curves obtained with the glass reference indicator electrode are completely superimposable, by movement of the potential ordinate, on the standard curves obtained with a saturated calomel half-cell and potassium sulphate salt bridge. Trouble may arise if the platinum reaction indicator electrode runs negative to glass, as the unscreened glass electrode is apt to give spurious potentials when the pH meter connections are reversed. Solutions with acid concentrations above normal can be titrated with the glass electrode, but this is not considered to be good practice, since most electrodes are subject not only to the acid error—

migration of H_3O^+ ions—in this range, but also to short-term vagaries and to drifts from which recovery is slow.

The behaviour of the silver reference indicator electrode varies with conditions. In group 1 reactions, its potential tends to follow that of the platinum reaction indicator electrode with a difference of some 670 mV (silver negative), so that it is polarised or acts after the

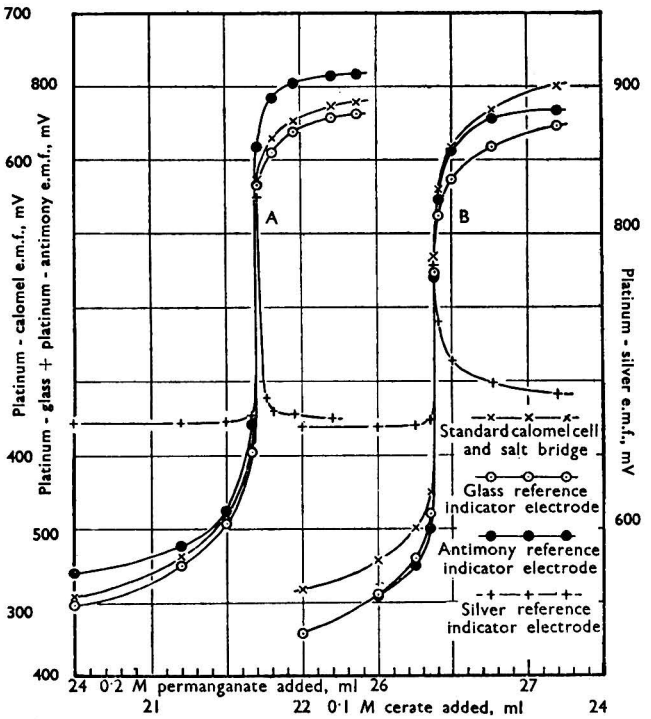

Fig. 1. Reactions of group 1. A, end-point curves for titration of iodide with permanganate; B, end-point curves for titration of iodide with cerate

fashion of an inert electrode. With powerful oxidants such as cerate and permanganate, the potential forms a peak exactly at the end-point (Fig. 1) and then returns towards its former value. This indication is reproducible and accurate, but the height attained by the peak may vary from 40 to 160 mV. A semblance of a normal form of end-point has been observed with iodate, but no indication at all occurs with ferricyanide or chloramine-T. In reactions of groups 2 and 3, when an excess of iodide ions is present, the silver - silver iodide electrode is presumably set up (very quickly), and the silver reference indicator electrode then functions excellently as a constant potential generator, giving normal curves of the usual sharpness that are superimposable on the curves obtained by the standard salt bridge - calomel cell method. Since the electrode circuit is all metal, its ohmic resistance is low and the potentiometer response is highly sensitive, except in reduced solutions, when the resistance rises and the response becomes sluggish. However, the uncertainty of measurement with the Tinsley potentiometer remains within 2 to 3 mV, which is much superior to the response with the salt bridge and calomel cell. No treatment such as scraping or activation is required between titrations, and the potentials are reproducible.

The behaviour of the antimony reference indicator electrode is complicated because it can exist in two forms: $Sb/Sb^{\cdot\cdot\cdot}$ (or Sb/Sb_2O_3) and $Sb/Sb^{\cdot\cdot\cdot\cdot\cdot}$ (or Sb/Sb_2O_5), with other possible forms of $Sb^{\cdot\cdot\cdot}/Sb^{\cdot\cdot\cdot\cdot\cdot}$ and Sb/Sb_2O_4. If preserved in one state or other, it acts as a constant potential generator and a stable reference indicator electrode; but in electron transfer reactions it is liable to change from one state to the other during the reaction. If converted to the higher valency form by oxidants, it does not retain this state on exposure

to air, but reverts, presumably by reaction between Sb and $Sb^{\cdots\cdots}$, to the lower valency form. The consumption of oxidant or reductant that must occur during conversion from one form to the other is small, being less than 0·01 ml of 0·1 *N* reagent for a fairly large electrode surface. In titration of iodine solutions by reductants no error is caused, as oxidant consumed by conversion to quinquivalency is repaid on reduction to tervalency. On moving from ter- to quinquivalency, the reference potential should rise, *i.e.*, the difference potential, platinum minus antimony, should fall as platinum is positive to antimony, whilst the converse

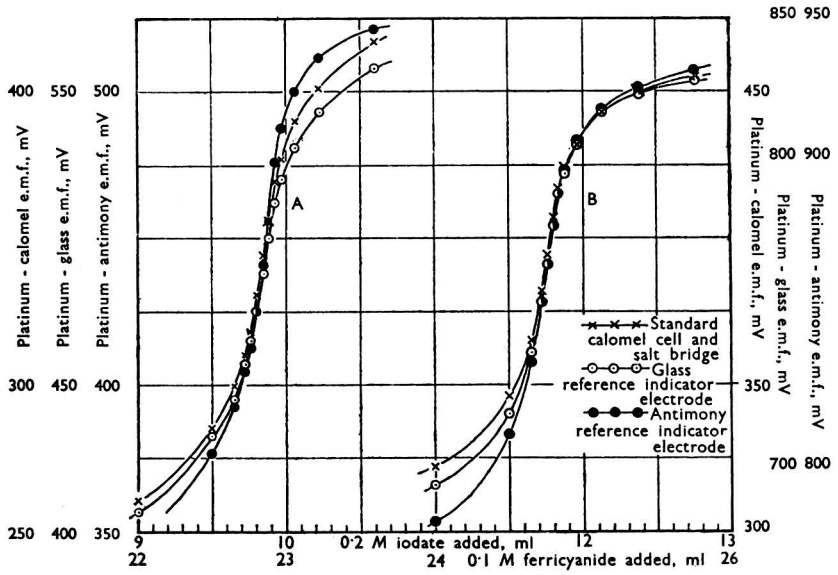

Fig. 2. Reactions of group 1. A, end-point curves for titration of iodide with iodate; B, end-point curves for titration of iodide with ferricyanide

should hold during the reverse motion. Initial equilibration of the antimony electrode depends upon the titration and the previous treatment of the electrode. The scraped electrode reaches equilibrium more quickly, since the appropriate valency state is deposited immediately, but it is unnecessary to scrape or clean the electrode between titrations as it reaches equilibrium with time enough to record the correct end-point even in the fastest titration. As the normal state is the tervalent, equilibrium is immediately reached in reducing solutions, and the electrode gives a steady reference potential in the titration of bivalent tin, thiosulphate and tervalent arsenic and antimony with standard iodine solution. After the end-point is passed, the electrode is fairly slowly changed to the quinquivalent condition and the platinum - antimony potential falls off (Fig. 3). In oxidising solutions, the quinquipositive form is produced so that the electrode potential rises to equilibrium in the titration of iodine by thiosulphate, arsenious or antimonous solutions, steadies when the end-point is approached, falls correctly at the end-point and becomes the steady reference terpositive value when the end-point is passed. In group 1 reactions, the electrode is brought up to the quinquivalent state and preserved therein, when it acts as a constant potential electrode. An anomalous effect in which the reference potential falls, causing a magnified potential change over the end-point, has occasionally been observed, particularly with chloramine-T. This is being further investigated. Again the negligible ohmic resistance of the electrode circuit gives a greatly increased sensitivity of potentiometer response over the calomel cell - salt bridge system, which reduces the uncertainty of measurement in reduced solutions to within 2 mV.

As in precipitation reactions[1] the reference indicator electrodes all show an increase in speed of equilibration over the calomel cell - salt bridge system. Reactions of group 1 are inherently slower than those of groups 2 and 3, and require 4 to 6 minutes for the potentials to reach equilibrium at the end-point with the calomel cell and salt bridge; the reference indicator electrodes require about half this time. With the platinum - glass electrode system measured on a pH meter, no change in sensitivity, *i.e.*, cell chain resistance, is noticeable,

as it is swamped by the high input impedance of the meter. With platinum - calomel, platinum - silver and platinum - antimony electrode systems metered on a low impedance potentiometer, the metering sensitivity suffers a sharp drop exactly at the end-point in titration of iodine by reductants on passing from high to low potentials, and remains insensitive in the presence of excess of reductant. A sudden increase takes place in reverse titrations. In terms of galvanometer deflection with a Tinsley 50-ohm per volt potentiometer and standard 1-metre taut-suspension mirror galvanometer at full sensitivity, the change is of the order

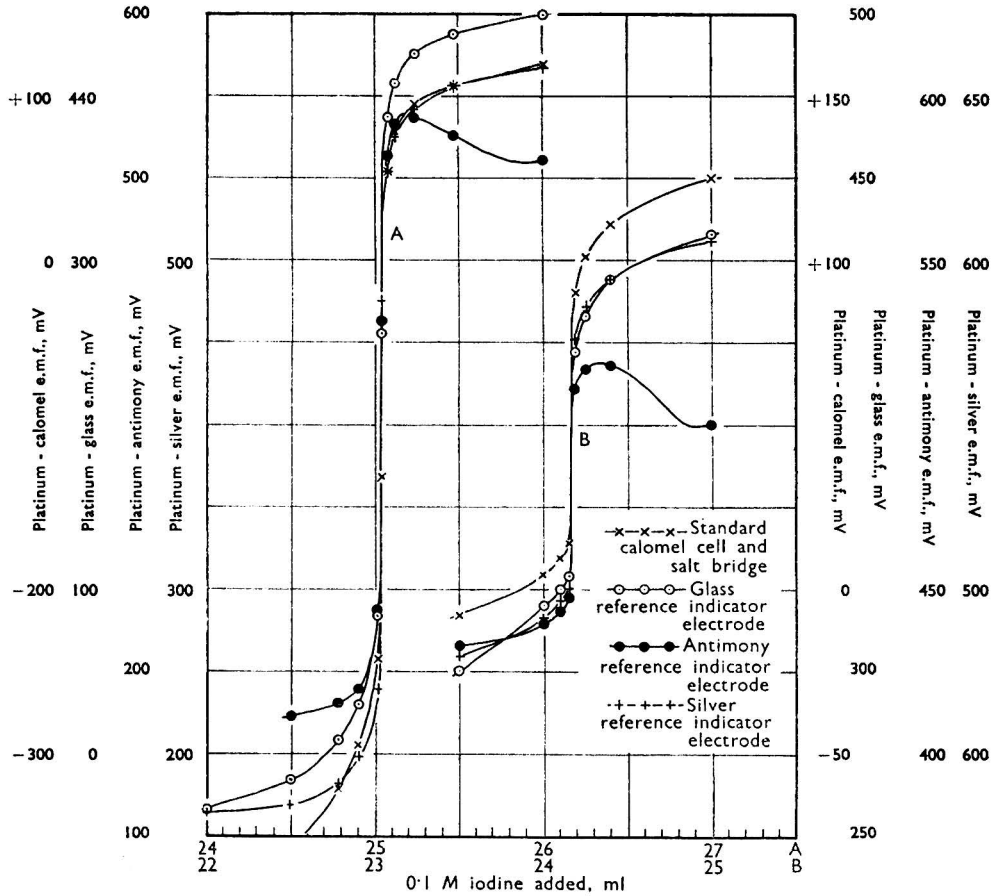

Fig. 3. Reactions of group 2. A, end-point curves for titration of tin^{II} in tartrate buffer with iodine; B, end-point curves for titration of arsenite in acetate buffer with iodine

of 0·05 to 50 mV per mm with calomel cell and salt bridge, 0·01 to 3 mV per mm with the silver reference indicator electrode and 0·01 to 2 mV per mm with the antimony reference indicator electrode. Since this applies to tin, antimony and arsenic titrations as well as to thiosulphate, irreversibility of the electrode is not a likely explanation. A sudden high resistance appears to be generated in the cell chain; it is the more marked the higher the ohmic resistance of the cell chain. Indeed, this sudden change in resistance can be used to locate the end-point accurately, but is so sharp and sudden that little preliminary warning is given. A similar, but less marked, increase in resistance occurs with the silver and calomel and to a lesser degree with the antimony electrodes in group 1 reactions at, and after, the end-point. There is a recovery in sensitivity well past the end-point.

In group 2 or 3 reactions involving arsenic or antimony, it is necessary to buffer the solution at a fairly high pH. Buffering is also necessary when the glass electrode is used for reference indicator purposes at a pH value of more than 2. The potential jumps are less

in acetate than in bicarbonate buffer (Fig. 4) as the normal potentials of the SbO_4'''/SbO_3''' and AsO_4'''/AsO_3''' redox systems increase with decreasing pH. Thiosulphate cannot be used safely in bicarbonate buffer as some oxidation to sulphate takes place, but in acetate

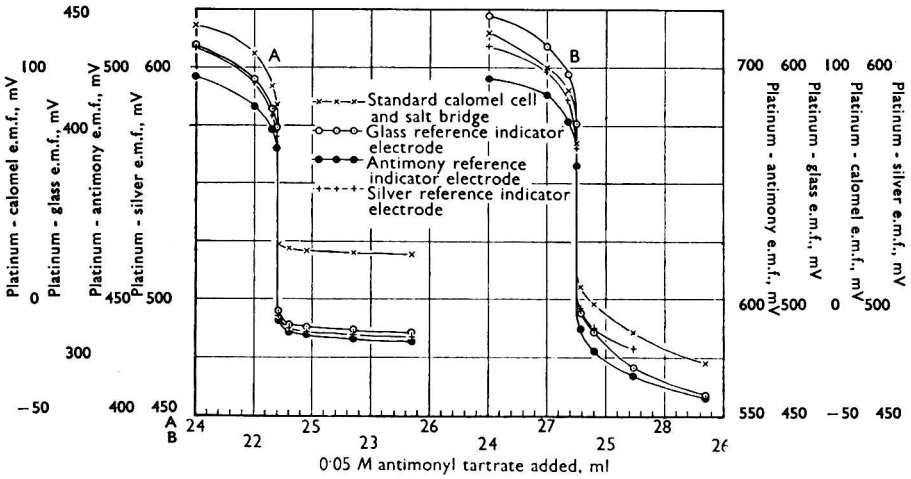

Fig. 4. Reactions of group 3. A, end-point curves for titration of iodine in acetate buffer with antimonyl tartrate; B, end-point curves for titration of iodine in bicarbonate buffer with antimonyl tartrate

buffer, free acetic acid, dilute sulphuric and hydrochloric acids, tartrate buffer and tartrate - bicarbonate medium results are excellent. Selenium, cuprous, chromic, zinc, manganous and cerous ions, either free or complexed (*e.g.*, as tartrate) are without influence; this allows determination of such materials as selenite, copper, hydrogen peroxide, sulphides, permanganate, cerate, dichromate, iodate, bromate, ferricyanide and vanadate by back-titration methods with arsenite or thiosulphate. Where such reactions, *e.g.*, selenite or dichromate, require acid concentrations higher than are acceptable to the glass electrode, the solution after liberation of iodine is treated with an excess of sodium acetate, or nearly neutralised with sodium hydroxide in the presence of tartaric acid; precipitation of potassium hydrogen tartrate, if potassium ion should be present in the system, does not interfere, although the abrading action of the stirred precipitate on the silver electrode causes momentary kicks in the platinum - silver potential.

The use of carbon tetrachloride to remove free iodine in reactions of group 1 is advantageous with oxidants of lower normal potential, such as ferricyanide, iodate and chloramine-T, and leads to smoother curves; but, to be effective, the solvent must be thoroughly dispersed in the solution. The iodine solution so formed is liable to cause surface corrosion and staining of the antimony electrode, which does not affect its action; but it seems desirable to clean the electrode after such an experiment.

Methods

Apparatus—

The apparatus has previously been discussed.[1] A Marconi mains-operated pH meter was used for measurements with Marconi glass electrodes, and a Tinsley 50-ohm per volt precision vernier potentiometer for other electrodes. Platinum and silver wire and thin cast antimony rod, all glass sheathed, formed the metal electrodes and a saturated calomel half-cell with a salt bridge of saturated potassium sulphate was used as the standard reference electrode. Several electrodes were studied simultaneously by multiple potentiometers. A magnetic stirrer driven by an induction motor was found to be more satisfactory than the original arrangement[1] and eliminated commutator interference and erratic speed variation. No interference from the magnetic fields, either on the electrodes or on the valve potentiometer, whose high input impedance renders it susceptible to interference pick-up, was observed. Magnetic rotors sealed in glass were used, as polythene is attacked by iodine. Times were

taken by stop-watch, and equilibration was regarded as complete when the potential did not alter in 1 minute.

REAGENTS—

Purified reagents were used throughout, and solutions were prepared by direct weighing when possible, calibrated glassware being used. Solutions were further checked by gravimetric and various standard volumetric procedures.

PROCEDURES AND RESULTS—

Since the procedures are well known, only brief experimental details are given, and the results are discussed under each heading.

REACTIONS OF GROUP 1: DIRECT TITRATION OF IODIDES—

Permanganate—Dilute an aliquot of standard 0·1 *M* iodide solution to 120 ml, add 15 ml of 2 *N* sulphuric acid and titrate with standard permanganate.[6,7] The accuracy of

TABLE I

TITRATION OF IODIDES WITH OXIDANTS*

Titrant	Amount taken	Found by calomel cell and salt bridge	Found by reference indicator electrodes		
			Glass	Silver	Antimony
Permanganate	5·01	5·01	5·01	5·01	5·00
	4·88	4·88	4·88	4·89	4·88
	4·90	4·90	4·90	4·90	4·90
	25·26	25·26	25·26	25·26	25·26
	25·19†	25·19	25·19	25·19	25·19
	24·97	24·96	24·96	24·96	24·95
	50·00	49·98	49·99	49·99	49·98
	49·66	49·66	49·67	49·67	49·66
	49·20	49·18	49·19	49·19	49·18
Cerate	5·01	5·01	5·01	5·02	5·00
	5·22	5·22	5·22	5·22	5·22
	4·90	4·91	4·91	4·92	4·89
	22·88†	22·88	22·88	22·88	22·88
	24·75	24·73	24·74	24·75	24·74
	25·26	25·26	25·26	25·27	25·26
	49·66	49·66	49·66	49·68	49·66
	49·20	49·18	49·19	49·19	49·19
	42·35	42·34	42·35	42·35	42·36
Iodate	9·90	9·90	9·90	9·95	—
	9·85†	9·84	9·85	—	9·85
	19·80	19·80	19·80	—	19·80
	20·21	20·20	20·21	—	20·19
	22·88	22·87	22·87	—	22·86
	49·20	49·18	49·19	—	49·18
	49·66	49·65	49·66	—	49·67
Ferricyanide	4·88	4·87	4·87	—	—
	5·01	5·00	5·00	—	—
	4·90	4·88	4·88	—	—
	24·75†	24·76	24·76	—	24·76
	25·18	25·18	25·18	—	25·19
	22·88	22·86	22·86	—	22·86
	50·00	50·01	50·02	—	50·01
	49·66	49·64	49·63	—	—

* Results expressed in milli-equivalents.
† End-point curves of these titrations are shown in Figs. 1 and 2.

the method has been extolled[8] and proposed for the standardisation of permanganate solutions. Attainment of equilibrium near the end-point has been found to take rather longer than previously indicated[8]; about 4 minutes with calomel cell and salt bridge and 2 to 3 minutes with glass, silver and antimony reference indicator electrodes. At and after the end-point, each increment of permanganate causes a rise in potential; the potential reaches a maximum

after 3 to 4 minutes, then as iodate forms the potential falls, reverting to its original value in a further 10 minutes. This has been found to continue long after the correct end-point has been passed if complete equilibrium is awaited after each drop. The results by the reference indicator methods are in excellent agreement with theory (Table I), and the curves with glass and antimony superimpose well on the standard calomel electrode curves. The silver curve is in the form of a peak (Fig. 1).

Cerate—Dilute an aliquot of standard iodide solution with water to 125 ml and titrate with standard 0·1 *M* sulphato-cerate solution[9] in *N* sulphuric acid solution.[10] Equilibrium

TABLE II

TITRATION OF REDUCTANTS WITH STANDARD IODINE SOLUTION*

Titration of	Amount taken	Found by calomel cell and salt bridge	Found by reference indicator electrodes		
			Glass	Silver	Antimony
Arsenite	5·23	5·23	5·23	5·23	5·23
	5·23	5·23	5·23	5·23	5·24
	4·98	4·98	4·98	4·98	4·98
	24·17†	24·17	24·17	24·17	24·17
	25·00	25·00	25·00	25·00	25·00
	24·90	24·88	24·89	24·88	24·90
	49·70	49·68	49·68	49·68	49·68
	49·20	49·21	49·20	49·21	49·21
	49·20	49·21	49·21	49·21	49·22
Antimonyl tartrate	5·00	5·00	5·00	5·00	5·00
	5·00	5·01	5·01	5·01	5·01
	4·92	4·92	4·92	4·92	4·93
	25·13	25·12	25·13	25·12	25·12
	25·13	25·11	25·12	25·12	25·12
	24·35	24·35	25·35	25·35	25·34
	48·61	48·59	48·60	48·60	48·61
	49·00	49·01	49·00	49·00	49·01
	49·00	49·01	49·01	49·01	49·00
Thiosulphate	25·75	25·76	25·75	25·76	25·76
	25·75	25·76	25·75	25·76	25·76
	24·38	24·38	24·38	24·38	24·38
	49·50	49·47	49·48	49·48	49·48
	49·50	49·48	49·47	49·48	49·49
	48·72	48·73	48·73	48·73	48·73
Stannous tin	5·63	5·61	5·61	5·61	5·61
	5·63	5·62	5·63	5·62	5·63
	25·04†	25·04	25·04	25·04	25·04
	25·04	25·03	25·03	25·03	25·03

* Results expressed in milli-equivalents.
† End-point curves of these titrations are shown in Fig. 3.

is attained in 5 minutes at the end-point with calomel, and in 2 minutes with glass, antimony and silver electrodes. Owing to the increase in acidity of the solution during titration, the curves of the glass and antimony reference indicator electrode systems diverge slightly from the standard calomel curve, but the end-points are excellent (Fig. 1) and the results accurate (Table I). The silver reference indicator electrode again gives a peak at the end-point.

Iodate—Dilute an aliquot of standard 0·1 *M* iodide solution to 100 ml, add 10 ml of 2 *N* sulphuric acid and 10 ml of carbon tetrachloride, and titrate with 0·02 *M* iodate solution.[11,12] Equilibration speed was about the same as for permanganate. The potential break is much smaller than with permanganate or cerate. The curves with glass and antimony are excellent (Fig. 2) and the results satisfactory (Table I). The silver electrode is unsatisfactory.

Chloramine-T—Titrations with chloramine-T will form the subject of a separate communication.

Ferricyanide—To an aliquot of 0·1 *M* iodide solution add 75 ml of a solution 0·2 *M* in acetic acid and 0·2 *M* in sodium acetate (later referred to as 0·2 *M* acetate buffer), 30 ml of 0·2 *M* zinc sulphate solution and 10 ml of carbon tetrachloride; dilute to 150 ml and titrate with 0·1 *M* ferricyanide solution.[13]

The electrodes can be cleaned by brief immersion in *N* sodium hydroxide solution and subsequent washing with water, acid and water. Equilibration was fairly rapid. The end-point is retarded in the absence of acetate buffer and organic solvent, and absorption of carbon dioxide by the unbuffered solution affects the glass and antimony electrode potentials. Silver gives a uniform potential without inflection. The curves are smooth (Fig. 2) and the results good (Table I).

REACTIONS OF GROUP 2: DIRECT TITRATION OF REDUCTANTS WITH STANDARD IODINE SOLUTION—

One acid concentration only has been investigated for each reductant.

Add 75 ml of 0·2 *M* acetate buffer solution to an aliquot of 0·1 *N* antimonyl tartrate, arsenious or thiosulphate solution, dilute to 125 ml with water, and titrate with standard

TABLE III

TITRATION OF STANDARD IODINE WITH REDUCTANTS*

Titrant	Medium	Amount taken	Found by calomel cell and salt bridge	Found by reference indicator electrodes		
				Glass	Silver	Antimony
Antimonyl tartrate ..	Bicarbonate buffer	5·00	5·01	5·01	5·01	5·01
		4·45	4·45	4·45	4·45	4·45
		4·45	4·45	4·45	4·45	4·45
		24·75†	24·76	24·76	24·76	24·76
		24·70	24·72	24·72	24·72	24·72
		25·69	25·68	25·68	25·68	25·68
	Acetate buffer	25·69	25·68	25·68	25·68	25·67
		25·69	25·67	25·67	25·67	25·67
		24·70†	24·70	24·70	24·70	24·70
		48·66	48·65	48·65	48·65	48·64
		45·99	45·99	46·00	46·00	45·98
		45·99	46·00	45·98	45·99	45·99
Arsenite	Bicarbonate buffer	25·69	25·70	25·69	25·69	25·69
		24·70	24·70	24·70	24·70	24·70
		24·70	24·71	24·70	24·70	24·71
		48·66	48·67	48·67	48·67	48·67
		48·66	48·64	48·64	48·64	48·65
	Acetate buffer	5·00	5·00	5·00	5·00	5·00
		5·00	5·00	5·00	5·00	5·00
		4·45	4·44	4·44	4·44	4·44
		25·69	25·68	25·68	25·68	25·68
		25·69	25·67	25·68	25·67	25·68
		24·75	24·76	24·76	24·76	24·76
Thiosulphate	Acetate buffer	4·45	4·45	4·45	4·45	4·45
		4·45	4·45	4·45	4·45	4·46
		5·00	5·01	5·00	5·00	5·00
		24·56	24·56	24·56	24·56	24·56
		24·56	24·55	24·55	24·55	24·55
		25·69	25·69	25·69	25·69	25·70
	Decinormal acid	24·50	24·50	24·50	24·50	24·50
		24·50	24·50	24·50	24·50	24·50
		25·69	25·68	25·68	25·68	25·68
		45·99	45·97	45·98	45·97	45·98
		45·99	45·96	45·97	45·97	45·96

* Results expressed in milli-equivalents.

† End-point curves of these titrations are shown in Fig. 4.

0·1 *M* iodine in 4 per cent. potassium iodide solution. For stannous tin (prepared in 2 *N* hydrochloric acid), add 5 g of tartaric acid, sufficient 5 *N* sodium hydroxide solution to neutralise the free acid and 5 g of sodium bicarbonate; dilute to 125 ml and titrate.

The antimony, arsenic and thiosulphate curves are much alike, so only one example is shown (Fig. 3), but the lower normal potential of the stannous - stannic electrode leads to a much larger potential jump (Fig. 3). Equilibration was rapid with all electrodes. Electrodes on the low impedance potentiometer show a high resistance, which vanishes sharply at the end-point. With the antimony reference indicator electrode, conversion to quinquivalency

occurs in excess of iodine, causing the difference potential to decrease, so that the curve falls off after passing the end-point (Fig. 3). Results are shown in Table II.

REACTIONS OF GROUP 3: TITRATIONS OF IODINE WITH REDUCTANTS—

(*i*) *Bicarbonate buffer*—Dissolve 5 g of sodium bicarbonate in water, add an aliquot of standard 0·1 *M* iodine solution, dilute to 125 to 150 ml and titrate quickly with 0·1 *N* reductant (0·05 *M* arsenite or antimonyl tartrate, 0·1 *M* thiosulphate).

(*ii*) *Acetate buffer*—Add an aliquot of standard iodine to 75 ml of 0·2 *M* acetate buffer, dilute to 125 to 150 ml, and titrate quickly with standard reductant.

(*iii*) *Decinormal acid*—Dilute 7·5 ml of 2 *N* sulphuric acid with water, add an aliquot of standard iodine, dilute to 125 to 150 ml and titrate quickly with standard thiosulphate.

With arsenite and antimonyl tartrate, the reaction is incomplete in acid solution, and with thiosulphate partial oxidation to sulphate causes low results in bicarbonate medium. With antimony and arsenic the potential break at the end-point is less in acetate buffer

TABLE IV

TITRATION OF LIBERATED IODINE WITH THIOSULPHATE*

Substance determined	Amount taken	Found by calomel cell and salt bridge	Found by reference indicator electrodes		
			Glass	Silver	Antimony
Permanganate	25·22	25·22	25·22	25·22	25·22
Cerate	27·44	27·44	27·44	27·44	27·45
Iodate	24·65	24·66	24·66	24·66	24·66
Ferricyanide	25·00	25·01	25·02	25·02	25·02
Dichromate	12·47	12·48	12·48	12·47	12·48
Selenite	22·10	22·08	22·08	22·07	22·09
Copper	38·72	38·72	38·72	38·72	38·725

* Results, expressed in milli-equivalents, are means of three replications.

than in bicarbonate buffer, as predicted, since the normal potential of antimonyl - antimonic and arsenious - arsenic electrodes rises with decreasing pH, but this is offset by a rather greater sharpness of end-point. The thiosulphate end-point shows little variation in decinormal acid, acetate buffer, 0·5 *N* acetic acid and tartrate buffer. As usual, the potentiometer sensitivity with a 50-ohm per volt Tinsley potentiometer is low on the reduced side, but excellent in an excess of iodine, the transition being smooth and sharp. Equilibration was rapid with all electrodes. Glass and silver reference indicator electrodes give normal smooth curves, and antimony, being converted to the quinquivalent form before the end-point, does not attain complete equilibrium, but joins the other curves at the end-point, giving the usual sharp drop. Since the curves are all much alike, one example only is given (Fig. 4); this shows the difference between bicarbonate and acetate buffers for antimony. The results are excellent (Table III).

Many procedures are based on the liberation of iodine from an excess of iodide and titration of the excess with arsenite or thiosulphate. Some of these reactions, *e.g.*, dichromate and selenite, require a high acid concentration for the initial stage, others, such as copper, permanganate, cerate and so on, will react completely at a pH of 1 or higher. In order to protect the glass electrode from excessive acidities, the liberation of iodine can be allowed to proceed in strong acid, and then the excess of acid is neutralised with alkali or removed with sodium acetate; if necessary in the presence of a complexing agent such as tartaric acid to prevent hydrolysis of metal ions with the formation of a precipitate that may adsorb iodine. Some examples are given below.

Permanganate, cerate, iodate—Work in a volume of 125 ml that is 0·1 *N* in sulphuric acid, and titrate the liberated iodine immediately.

Ferricyanide—Work in a volume of 125 ml, containing 30 ml of 0·2 *M* zinc sulphate and 75 ml of 0·2 *M* acetate buffer, and titrate the liberated iodine immediately.

Dichromate—Work in 2 *N* hydrochloric acid, set aside for 3 minutes, add 5 g of tartaric acid, dilute to 150 ml, add the calculated amount of 5 *N* sodium hydroxide to neutralise the mineral acid and half the tartaric acid, and titrate the liberated iodine immediately.

Selenite—Work in 2 *N* hydrochloric acid, set aside for 2 minutes, add 8 g of sodium acetate, dilute to 150 ml and titrate the liberated iodine immediately. The solution must

be vigorously stirred near the end-point to desorb iodine from the flocculated precipitate of selenium.

Copper—Treat the sample in a volume of 125 ml containing 5 ml of glacial acetic acid with 5 g of potassium iodide in a little water and titrate immediately.

The curves are all satisfactory and similar to the normal thiosulphate - iodine curves, which shows that there is no interference from the reaction products, *i.e.*, no seleniding or copper plating of the silver or antimony; the results are excellent (Table IV). Individual graphs are not shown, as they are similar to those in Fig. 4.

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Methods for Detecting the End-Point in the Titration of Iodine with Thiosulphate

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A simple amperometric circuit proved the best indicator of the end-point in the titration of iodine with thiosulphate. Starch indicator can lead to errors, on the low side, of the order of 20 to 40 micrograms of iodine in volumes of 50 to 200 ml, and sodium starch glycollate is even less accurate. The dead-stop end-point method and the derivative polarographic method are both less satisfactory than the amperometric method.

To determine the most suitable method for the detection of the end-point in the titration of iodine with thiosulphate five methods were tried. Two depended on a colour change, the indicators being starch and sodium starch glycollate, and three were electrical: an amperometric method, the dead-stop end-point method, and a derivative polarographic method.

So far as is known, the simple circuit used for the amperometric method has not before been described for this titration, although Harris and Lindsey[1] and Laitinen and Burdett[2] used similar but rather more complex arrangements.

During the past 25 years several workers have used the dead-stop end-point procedure for titrating iodine with thiosulphate; different values, up to 150 millivolts, have been recommended for the potential difference to be applied. In one paper[3] the method is reported to be unsatisfactory for microgram amounts of iodine.

The circuit used here for the derivative polarographic titration was that recently devised by Reilley, Cooke and Furman,[4] who have given a full account of the theory of the method. A constant current of the order of 2 micro-amperes is passed between two platinum electrodes and the potential difference between them is measured by a potentiometer or valve voltmeter.

The potential difference depends on the slope of the polarogram of the solution at the point where it crosses the zero current line, and is higher, in the present titration, when iodine is virtually absent than when it is present in microgram or even larger amounts. The use of this method for titration of iodine has not been reported hitherto.

With the electrical methods it is more convenient, although no more accurate, to add an excess of standard sodium thiosulphate solution and titrate the excess with potassium iodate solution. For this, the solution to be titrated must be acid; about 0·15 *N* acid is suitable, although the concentration is not critical.

Sodium thiosulphate solutions are more stable if made from water freed from carbon dioxide; even so, a 0·0025 *N* solution should be checked daily against potassium iodate.

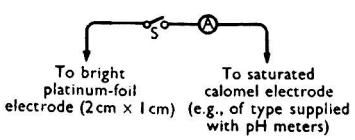

Fig. 1. Circuit for amperometric titration. A, micro-ammeter, F. S. D. 5 μA (that used had a resistance of 3000 Ω). S, on-off switch

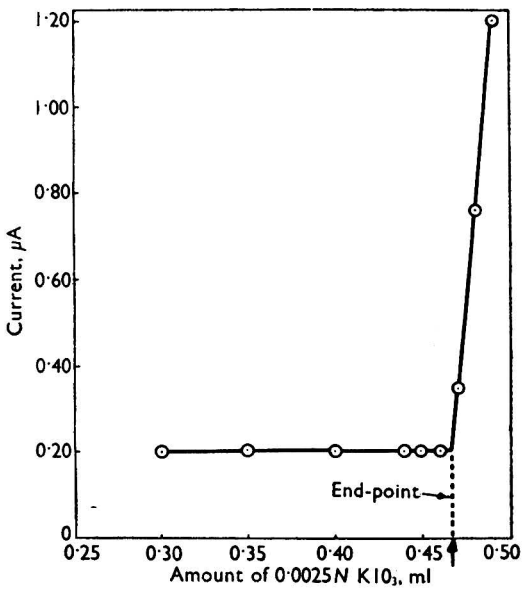

Fig. 2. Results of amperometric titration

Standard potassium iodate solutions were prepared from analytical grade potassium iodate heated to 120° C for 2 hours and cooled in a desiccator. A known weight was dissolved in distilled water and made up to a known volume at 20° C; grade-A glassware calibrated at 20° C was used.

Except where noted, the volumetric glassware used consisted of grade-A pipettes (checked for sufficient precision by weighing deliveries of distilled water) and a grade-A 1-ml burette, graduated for 8 inches of its length at 0·01-ml intervals, with the delivery tip drawn out to a fine point. Titrations of the excess of thiosulphate with potassium iodate solution were made, each being less than 1 ml.

Iodine can be lost, presumably by volatilisation, at a rate sufficient to affect accurate work; it is also formed in an acid solution of potassium iodide. With amperometric titration the loss of titre was found to be 6 μg of iodine per minute from 50 ml of 0·0025 *N* iodine solution containing 0·7 per cent. by weight of potassium iodide and 5 ml of 1·5 *N* sulphuric acid, when continuously stirred in a 100-ml beaker in daylight. Owing to the formation of iodine, 50 ml of a solution containing 0·7 per cent. by weight of potassium iodide and 5 ml of 1·2 *N* sulphuric acid was found to increase in titre by about 2 μg of iodine per minute.

Methods, Apparatus and Reagents

Colorimetric methods—

The indicators used in the two methods were—

(1) A 1·0 per cent. solution of analytical grade soluble starch in distilled water.
(2) A 1·0 per cent. solution of sodium starch glycollate in distilled water.

AMPEROMETRIC TITRATION—

Procedure—Fit up the circuit shown in Fig. 1. Place both electrodes in the solution, which must be mechanically stirred. Add sufficient iodine-free analytical grade potassium iodide to ensure at least 0·4 per cent. by weight is present at the end of the titration. Add sufficient dilute sulphuric acid to make the solution about 0·15 *N* in acid at the end of the titration. Add an excess of standard sodium thiosulphate solution. Close the amperometric circuit and titrate with standard potassium iodate solution until the first permanent increase of current (see Fig. 2) shows that the end-point has been reached.

Alternatively, after placing the electrodes in the mechanically stirred solution, add sufficient iodine-free analytical grade potassium iodide to ensure at least 0·4 per cent. by weight at the end of the titration. Add acid, if necessary, to make the solution at least 0·15 *N* in sulphuric acid at the end of the titration; titrate with standard sodium thiosulphate solution. Close the amperometric circuit when approaching the end-point and continue to add sodium thiosulphate solution until the current is unchanged by further additions.

In most applications the first procedure is easier and quicker.

DEAD-STOP END-POINT TITRATION—

Procedure—Fit up the circuit shown in Fig. 3. The method requires a small potential difference between two platinum electrodes. Authorities differ as to the voltage to be used, values up to 150 millivolts having been recommended; in the circuit recommended here the operator can adjust the voltage to any suitable value.

Place both electrodes in the solution, which must be mechanically stirred. Add sufficient iodine-free analytical grade potassium iodide to ensure at least 0·4 per cent. by weight is present at the end of the titration.[5] Add sufficient dilute sulphuric acid to make the solution about 0·15 *N* in acid at the end of the titration. Add an excess of standard sodium thiosulphate solution. Close the circuit and adjust the potentiometer until the millivoltmeter indicates the value required (say 50 millivolts). Titrate with standard iodate solution until an increase in current shows that the end-point has been reached.

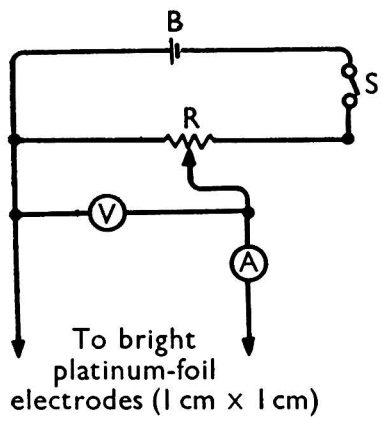

Fig. 3. Circuit for dead-stop end-point titration. A, micro-ammeter, F.S.D. 5μA (that used had a resistance of 3000 Ω); B, a 1·5-V dry battery; R, potentiometer (47 Ω); S, on-off switch; V, millivoltmeter

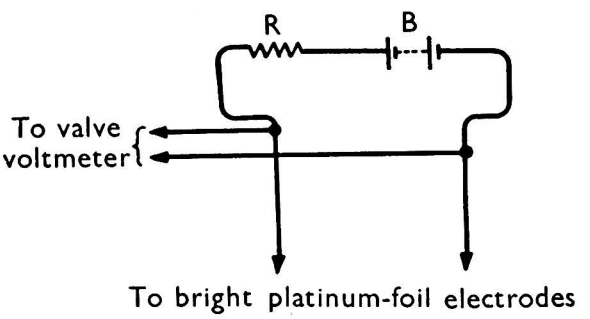

Fig. 4. Circuit for derivative polarographic titration. B, a 45-V dry battery (as used in hearing aids); R, about 20 MΩ, carbon, ¼ watt

DERIVATIVE POLAROGRAPHIC TITRATION—

For this method all that is required is a pH meter (of the type that can be used as a valve voltmeter), a small dry H.T. battery, an inexpensive resistance and two platinum electrodes.

Insufficient experience has been gained with this method for this titration to make available detailed directions for the procedure. In the tests made the circuit shown in Fig. 4 was used. The solution of iodine containing 0·7 per cent. w/v of potassium iodide and 4 ml

of 1·5 *N* sulphuric acid was mechanically stirred in a beaker. An excess of standard sodium thiosulphate solution was added, the electrodes were immersed, and standard potassium iodate solution added until the potential began to decrease, as shown by the broken line in Fig. 5. This indicated that the end-point had been reached; the volume in the beaker at the end was about 40 ml.

Results

Comparison of starch and amperometric titrations—

The sensitivities of end-point indication by these two methods were compared as follows, all titrations being made at about 18° C. To each of two 50-ml portions of distilled water were added 4 ml of 2 *N* sulphuric acid and 0·5 g of iodate-free potassium iodide. To one portion was added 0·5 ml of a 1 per cent. solution of analytical grade soluble starch, and then 0·0025 *N* iodine solution, 0·01 ml at a time, in a good light. No blue colour could be seen by a practised observer until 0·07 ml had been added. In the other portion the electrodes of the amperometric titration apparatus were immersed; a steady current of 0·6 micro-ampere resulted. Addition of 0·01 ml of the 0·0025 *N* iodine solution immediately gave a steady current of 1·2 micro-amperes, which increased to a steady 1·8 micro-amperes on addition of a further 0·01 ml of iodine solution.

The 0·0025 *N* iodine solution was made by diluting a more concentrated solution prepared by dissolving 13·0 g of analytical grade iodine in a solution of 25 g of analytical grade potassium iodide in 30 ml of water and making up to 1 litre. Water re-distilled from glass was used throughout and all solutions were kept in the dark. The concentration of the final solution of iodine was found to be 0·0025 *N* by titration with 0·0025 *N* sodium thiosulphate solution standardised against 0·0025 *N* potassium iodate solution; the amperometric end-point was used in these standardisations.

In a similar test two 200-ml portions of distilled water were taken and to each were added 20 ml of 2 *N* sulphuric acid and 2 g of iodate-free potassium iodide. To one portion was added 0·5 ml of a 1 per cent. solution of soluble starch; 0·16 ml of 0·0025 *N* iodine solution was then required to give a blue colour detectable by eye. The electrodes of the amperometric titration apparatus were immersed in the other portion; 0·01 ml of 0·0025 *N* iodine solution gave a definite increase in the steady current.

The same order of difference in the end-point indications given by the two methods was observed in the titration of two 50·00-ml portions of 0·0025 *N* potassium iodate solution to each of which had been added, in turn, 0·7 g of iodate-free potassium iodide, 4 ml of 2 *N* sulphuric acid and 50·00 ml of sodium thiosulphate solution, slightly stronger than 0·0025 *N*. For the starch end-point 0·5 ml of a 1 per cent. solution of soluble starch was added. This experiment was repeated six times and gave the following results—

Volumes of 0·0025 *N* potassium iodate required in separate titrations of six portions with starch, ml—0·17, 0·19, 0·21, 0·20, 0·19, 0·20; average 0·19.

Volumes of 0·0025 *N* potassium iodate required in separate amperometric titrations, ml—0·11, 0·11, 0·11, 0·15, 0·14, 0·12; average 0·12.

Sodium starch glycollate titrations—

Sodium starch glycollate was suggested as an alternative to starch by Peat, Bourne and Thrower[6]; it has the great advantage that it can be added at any stage in the titration.

The sensitivity of this indicator appears to be rather less than that of starch. For example, in one test two 10·00-ml portions of 0·01 *N* potassium iodate solution were each diluted to 100 ml with distilled water, and to each was added 10 ml of 2 *N* sulphuric acid and 0·7 g of iodate-free potassium iodide. To one portion was added 0·6 ml of a 0·5 per cent. solution of sodium starch glycollate; the iodine was then titrated with 0·01 *N* sodium thiosulphate solution. The other portion was titrated with 0·01 *N* sodium thiosulphate solution, 0·3 ml of 1 per cent. starch solution being added shortly before the end-point was reached. Comparison of the results showed that the blue colour in the sodium starch glycollate titration disappeared after slightly less sodium thiosulphate solution had been added than in the starch titration. A grade-A 10-ml burette with 0·02-ml graduations was used; the graduated portion was 22 inches long. The results for four pairs of titrations were as follows—

Volumes of 0·01 *N* sodium thiosulphate with sodium starch glycollate, ml—9·74, 9·76, 9·78, 9·76; average 9·76.

Volumes of 0·01 *N* sodium thiosulphate with starch, ml—9·80, 9·80, 9·82, 9·80; average 9·81.

The titrations with sodium starch glycollate were repeated with 0·3, 1·0 and 1·5 ml of the 0·5 per cent. solution of sodium starch glycollate; there was little change in the result.

DEAD-STOP END-POINT TITRATION—

In the present work with dead-stop end-point titration it was sometimes found that reproducibility could not be attained with new electrodes or electrodes that had been standing in nitric acid for a long period; reproducibility with these electrodes improved greatly after

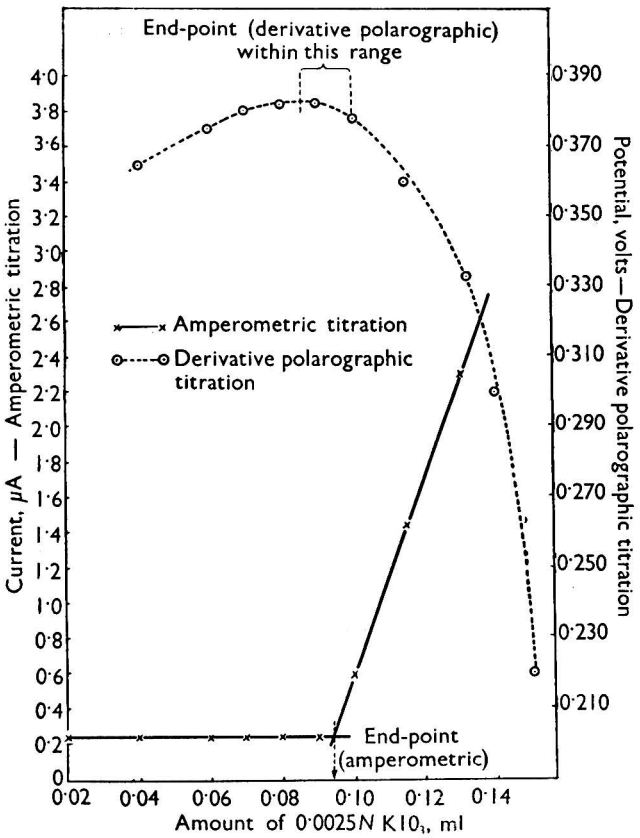

Fig. 5. Comparison of end-point indications by amperometric titration and derivative polarographic titration

a few determinations. (By contrast, the amperometric method described above gave reproducible results no matter what had been the history of the platinum electrode.) Potential differences of 20, 50 and 150 millivolts were tried; reproducibility was poor with the first of these.

Separate titrations were made with 0·0025 *N* potassium iodate solution by the amperometric and dead-stop end-point methods on identical samples, each prepared by adding 20·00 ml of sodium thiosulphate solution slightly stronger than 0·0025 *N* to a solution of iodine produced by adding 20·00 ml of 0·0025 *N* potassium iodate solution to 4 ml of 2 *N* sulphuric acid containing 0·5 g of iodate-free potassium iodide. Table I shows the results, expressed as millilitres of the sodium thiosulphate solution equivalent to 20·00 ml of 0·0025 *N* potassium iodate solution.

From Table I it is clear that results with the dead-stop end-point method vary with the applied potential difference. The method also appears to give a slightly less sensitive indication of the presence of iodine than the amperometric method.

DERIVATIVE POLAROGRAPHIC TITRATION—

Little experience in this method has been gained from our work. However, the results of a comparison of its end-point indication with that of the amperometric titration, shown in Fig. 5, appear to show that, although not so precise as the latter, it may be capable of giving the end-point with a possible error of $\pm 0{\cdot}01$ ml of $0{\cdot}0025\ N$ iodine solution ($\pm 3\ \mu$g of iodine)

TABLE I

COMPARISON OF AMPEROMETRIC AND DEAD-STOP END-POINT METHODS

Method	Amounts of thiosulphate used, ml	Mean, ml
Amperometric	19·43, 19·44, 19·43, 19·44	19·44
Dead-stop end-point, P.D. 20 millivolts ..	19·46, 19·42, 19·42, 19·39	19·42
" P.D. 50 millivolts ..	19·41, 19·43, 19·43, 19·43	19·43
" P.D. 150 millivolts ..	19·39, 19·38, 19·36, 19·40	19·38

when the volume is about 40 ml. The two graphs of Fig. 5 were plotted simultaneously for the same 40 ml of sodium thiosulphate solution (containing 4 ml of $1{\cdot}5\ N$ sulphuric acid and 0·5 g of potassium iodide) during titration with $0{\cdot}0025\ N$ potassium iodate solution.

CONCLUSIONS

Of the five methods tried, the amperometric is the most satisfactory. The simple circuit described, incorporating a pointer micro-ammeter, detects one microgram of iodine in 40 ml of solution.

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August 21st, 1952

The Determination of Antimony in Aromatic Organic Compounds Containing Nitrogen, Chlorine and Antimony

By N. T. WILKINSON

A method has been devised for determining antimony in organic compounds that also contain nitrogen and chlorine. The organic matter is destroyed by wet digestion with nitric and sulphuric acids, and the antimony compound formed is dissolved in a mixture of hydrobromic acid and bromine. The antimony is reduced by sulphurous acid, the excess of sulphur dioxide being removed by boiling, and determined volumetrically by titration with standard potassium bromate solution. The antimony can also be precipitated as the sulphide, separated by filtration, brought into solution and titrated.

Decomposition of the organic compound by fusion with sodium peroxide, cane sugar and potassium nitrate in a Parr bomb is not satisfactory, as an antimony compound is formed that is insoluble in dilute nitric acid or dilute hydrochloric acid. The method has been tested by determining antimony in synthetic mixtures of potassium antimony tartrate solutions and organic compounds containing nitrogen and chlorine.

We have had occasion to determine antimony in organic compounds containing approximately 30 per cent. of antimony in addition to chlorine and nitrogen. In order to bring the antimony into a condition suitable for its quantitative determination, it seemed best to destroy the organic matter by wet digestion with sulphuric and nitric acids. Nevertheless, the possibility of fusion in a Parr bomb with sodium peroxide, cane sugar and potassium nitrate mixture was also examined.

The Parr bomb fusion method was not successful, as a compound of antimony was formed that was insoluble in moderately strong hydrochloric acid. The fusion product was also insoluble in nitric acid. Wet digestion of the organic compound with nitric and sulphuric acids gave a clear solution; but on adding water and evaporating to remove residual nitric acid a precipitate formed that was insoluble in either sulphuric acid or a mixture of sulphuric and nitric acids. An insoluble precipitate was also produced when potassium antimony tartrate was similarly treated with nitric and sulphuric acids and the resulting solution diluted with water.

Unsuccessful attempts were made to dissolve the precipitate formed in the wet digestion of potassium antimony tartrate in (*a*) hydrochloric acid, (*b*) tartaric acid, (*c*) potassium hydroxide, and (*d*) tartaric acid followed by an excess of potassium hydroxide. However, it was completely soluble in a solution of bromine in hydrobromic acid, a solution similar to that used by Cotton[1] in the determination of silicon in iron. The bromine was then destroyed and the antimony reduced with sulphurous acid. The excess of sulphur dioxide was removed from the solution by boiling, and the antimony finally determined by titration with potassium bromate.

In the preliminary stages of the work bromine was removed from the solution by boiling before reducing the antimony with sulphur dioxide. It was occasionally found, however, that during the boiling, antimony was precipitated; the precipitate could be dissolved in tartaric acid, but the acid prevented the complete reduction of the antimony by sulphur dioxide. Antimony can be separated as the sulphide and dissolved, after filtration, in a mixture of hydrochloric acid, bromine water and hydrogen peroxide, and determined volumetrically. This procedure is recommended for the separation of antimony from certain other elements, such as iron, the presence of which would interfere with the bromate titration. Arsenic can be determined by titration with potassium bromate solution and is also precipitated by hydrogen sulphide. If both arsenic and antimony are present they must be separated.

The chlorine and nitrogen in the organic compounds were shown to have no effect on the determination after wet digestion with nitric and sulphuric acids by determinations of antimony in synthetic mixtures of potassium antimony tartrate solutions and the organic compounds specified.

Experimental

Throughout the experimental work a solution of potassium antimony tartrate was used. This was prepared by dissolving 13·34 g of anhydrous potassium antimony tartrate in distilled water in a calibrated flask and diluting to 500 ml. The antimony content was determined by titration with 0·05 *N* potassium bromate solution. (10 ml ≡ 0·1 g of antimony.)

Solution of the precipitate—

Ten-millilitre aliquots of the potassium antimony tartrate solution were treated with nitric and sulphuric acids by the direct procedure described on p. 168. The resulting solutions, each of which contained a white precipitate, were treated in one of the following ways in an attempt to dissolve the precipitate.

(*i*) Diluted to 100 ml with distilled water with 5 g of tartaric acid added.
(*ii*) Diluted to 100 ml with distilled water, with an excess of potassium hydroxide added.
(*iii*) Diluted to 100 ml with distilled water, with 5 g of tartaric acid added, followed by an excess of potassium hydroxide.

None of these treatments caused the white precipitate to dissolve.

(*iv*) Addition of 20 ml of a solution of bromine in hydrobromic acid (prepared by adding 10 ml of liquid bromine to 100 ml of hydrobromic acid, sp.gr. 1·48) and warming brought the white precipitate into solution.

Antimony content of the precipitate—

To determine if all of the antimony was contained in the white precipitate, four aliquots of the potassium antimony tartrate solution were treated with nitric and sulphuric acids by the direct procedure described on p. 168. Each solution was then diluted with 50 ml of water, heated to boiling and cooled. The solutions were filtered through weighed sintered-glass crucibles, of No. 4 porosity, and the precipitates washed with water. Each was dried at 100° C for 2 hours, cooled and weighed.

Weight of dried precipitate, g: (*a*) 0·0456, (*b*) 0·0908, (*c*) 0·0476, (*d*) 0·1348

The filtrates were each diluted to 250 ml, 5 g of sodium sulphite were added and dissolved, and the solutions set aside for 1 hour.

Ten millilitres of hydrochloric acid, sp.gr. 1·18, were added to each and the solutions were boiled until free from sulphur dioxide. No solution was allowed to evaporate to less than 150 ml; if all the sulphur dioxide had not been removed when this volume was reached, a further 100 ml of water were added and boiling was continued. When the solutions were free from sulphur dioxide they were titrated hot with 0·05 *N* potassium bromate solution, 1 drop of methyl orange being added as indicator.

Results—Throughout the work the weight of antimony has been calculated from the volume of standardised bromate solution used for titration according to the stoicheiometric reaction—

$$2KBrO_3 + 3Sb_2O_3 = 2KBr + 3Sb_2O_5.$$

The first drop of bromate in excess decolorises the methyl orange indicator.

The following antimony contents were obtained from the four filtrates after this treatment—

Filtrate	(*a*)	(*b*)	(*c*)	(*d*)
Amount of 0·05 *N* $KBrO_3$, ml	22·3	11·5	22·9	3·1
Antimony, g	0·0679	0·0350	0·0697	0·0094

Equal amounts (0·07 g) of the dried precipitates (*b*) and (*d*) were mixed each with 15 g of sodium peroxide, 1·45 g of potassium nitrate and 0·45 g of cane sugar, and each mixture was fused in a Parr bomb. The cooled melt was treated with water and acidified with dilute sulphuric acid. A large proportion of the precipitate remained undissolved.

The fusion was repeated, and after treating the cooled melt with water the solution was acidified with hydrochloric acid. A large proportion of the precipitate still remained undissolved.

COMPARISON OF THE PROCEDURES—

Four different aliquots of the potassium antimony tartrate solution were treated as described for the direct determination on p. 168. After titration with 0·05 *N* potassium bromate solution the antimony was precipitated as antimony sulphide and the antimony determined by the second procedure, p. 168. The results shown in Table I have been corrected for a blank test carried out on the reagents used.

TABLE I

RESULTS FOR POTASSIUM ANTIMONY TARTRATE ALONE BY THE PROPOSED PROCEDURES

	Direct determination		Determination after precipitation as sulphide	
Antimony added, g	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g
0·0250	8·25	0·0251	8·25	0·0251
0·0500	16·50	0·0502	16·42	0·0500
0·0750	24·60	0·0749	24·65	0·0750
0·1000	32·77	0·0998	32·72	0·0996

The end-point was sharper in the titrations of the solutions after separation as antimony sulphide. The blank was about 0·3 ml of 0·05 *N* potassium bromate solution in the direct titration and 0·05 ml in the titration after separation as sulphide.

MODIFIED PROCEDURE FOR LARGER AMOUNTS OF ANTIMONY—

Four aliquots of the potassium antimony tartrate solution representing 0·05, 0·10, 0·15 and 0·20 g of antimony were treated as described for the direct determination, p. 168, up to and including the addition of 150 ml of sulphurous acid. Each solution was then diluted to 200 ml in a measuring flask. During this dilution a precipitate formed in the solutions containing 0·15 and 0·20 g of antimony, which rapidly dissolved on mixing.

One hundred-millilitre aliquots of each solution were boiled free from sulphur dioxide as described in the procedure and finally titrated.

After titration the antimony was precipitated as the sulphide and determined as described on p. 168. The results shown in Table II have been corrected for a blank test carried out on the reagents used.

TABLE II

RESULTS FOR POTASSIUM ANTIMONY TARTRATE ALONE BY THE MODIFIED PROCEDURE FOR LARGER AMOUNTS OF ANTIMONY

	Direct determination		Determination after precipitation as sulphide	
Antimony added in 100-ml aliquot from 200 ml of solution, g	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g
0·0250	8·30	0·0253	8·27	0·0252
0·0500	16·46	0·0501	16·40	0·0499
0·0750	24·80	0·0755	24·80	0·0755
0·1000	32·73	0·0996	32·70	0·0995

DETERMINATION IN PRESENCE OF COMPOUNDS CONTAINING NITROGEN AND CHLORINE—

Aliquots of the potassium antimony tartrate solution were taken and known weights of *p*-chloraniline, aniline hydrochloride, and pyridine hydrochloride were added both separately and together. The organic matter was destroyed and the antimony determined by the direct procedure, p. 168. After treatment the antimony was precipitated as the sulphide and determined by the second procedure.

METHOD

REAGENTS—

Potassium bromate—A 0·05 *N* solution. Dissolve 1·392 g of potassium bromate in water, dilute to 1 litre, and standardise against standard arsenious oxide.[2]

Hydrobromic acid - bromine solution—Dissolve 10 ml of bromine in 100 ml of hydrobromic acid, sp.gr. 1·48. Heat the mixture slightly to dissolve the bromine completely.

PROCEDURE—

Direct determination—Weigh accurately a sample containing about 0·1 g of antimony and place it in a 400-ml beaker. Add 2 ml of water, 5 ml of sulphuric acid, sp.gr. 1·84, 2 ml of nitric acid, sp.gr. 1·42 and heat the mixture on a sand-bath until white fumes of sulphur trioxide appear.

Cool the solution, add 1 ml of nitric acid and again heat on the sand-bath until white fumes of sulphur trioxide appear. Add two further 1-ml portions of nitric acid, evaporating

TABLE III

RESULTS IN PRESENCE OF COMPOUNDS CONTAINING NITROGEN AND CHLORINE

		Direct determination		Determination after precipitation as sulphide	
Antimony added, g	Compounds added	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g	Amount of 0·05 *N* $KBrO_3$, ml	Antimony found, g
0·1000	*p*-Chloraniline (0·4 g)	32·9	0·1001	32·8	0·0998
0·1000	*p*-Chloraniline (0·2 g)	32·7	0·0995	32·7	0·0995
0·1000	Aniline hydrochloride (0·4 g)	32·9	0·1001	32·8	0·0998
0·1000	Aniline hydrochloride (0·2 g)	32·9	0·1001	32·8	0·0998
0·1000	Pyridine hydrochloride (0·4 g)	32·9	0·1001	32·9	0·1001
0·1000	Pyridine hydrochloride (0·2 g)	32·9	0·1001	32·8	0·0998
0·0250	*p*-Chloraniline (0·2 g), Aniline hydrochloride (0·2 g) and Pyridine hydrochloride (0·2 g)	8·35	0·0254	8·23	0·0251
0·0500	*p*-Chloraniline (0·2 g), Aniline hydrochloride (0·2 g) and Pyridine hydrochloride (0·2 g)	16·35	0·0498	16·20	0·0493
0·0750	*p*-Chloraniline (0·2 g), Aniline hydrochloride (0·2 g) and Pyridine hydrochloride (0·2 g)	24·52	0·0746	24·40	0·0743
0·1000	*p*-Chloraniline (0·2 g), Aniline hydrochloride (0·2 g) and Pyridine hydrochloride (0·2 g)	32·75	0·0997	32·63	0·0993

on the sand-bath to the appearance of white fumes of sulphur trioxide after each addition. If the organic matter is not completely destroyed after this treatment add more nitric acid and evaporate until the solution becomes colourless.

To the cooled solution add 5 ml of water and evaporate on the sand-bath until white fumes of sulphur trioxide appear. Repeat the addition of water and the evaporation twice more.

To the solution, which should now contain a white deposit, add 20 ml of hydrobromic acid - bromine solution and gently warm the mixture; this treatment quickly dissolves the antimony compound. Cool the solution, add 150 ml of sulphurous acid (water saturated with sulphur dioxide) and set aside for 1 hour.

Add 10 ml of hydrochloric acid and 100 ml of water and boil the solution to remove sulphur dioxide. Do not allow the volume of the solution to fall below 150 ml, and if all the sulphur dioxide is not removed when the solution reaches this volume, add a further 100 ml of distilled water and continue to boil.

When the sulphur dioxide is removed add 1 drop of methyl orange and titrate the hot solution with 0·05 *N* potassium bromate to the disappearance of the methyl orange colour.

1 ml of 0·05 *N* potassium bromate solution ≡ 0·003044 g of antimony.

Determination after separation as antimony sulphide—Proceed as described above to the point when sulphur dioxide has been removed. Saturate the solution so obtained with hydrogen sulphide, and pass the gas for 15 minutes while cooling the solution.

Immediately filter the precipitate of antimony sulphide and wash it with water saturated with hydrogen sulphide until it is free from halide. Place a clean beaker under the filter funnel, pierce a small hole in the bottom of the filter-paper and wash the antimony sulphide

through with water from the jet of a wash bottle. Use only about 25 to 30 ml of water in washing the antimony sulphide from the filter. Dissolve any remaining trace of precipitate from the filter-paper by pouring on to the filter a hot mixture consisting of 20 ml of hydrochloric acid, sp.gr. 1·18, 4 ml of 20-volume hydrogen peroxide and 10 ml of saturated bromine water. Wash the filter a few times with water (the final volume of the solution should be approximately 100 ml). Add 10 drops of bromine and heat the mixture to boiling to completely dissolve the antimony sulphide. Continue boiling for a few minutes to remove most of the bromine. Cool the solution, add 150 ml of sulphurous acid and set aside for 1 hour.

Boil the solution to remove sulphur dioxide; if the sulphur dioxide is not completely removed when the volume of the solution is reduced to 150 ml, add 100 ml of water and continue boiling.

When the solution is free from sulphur dioxide, add 1 drop of methyl orange and titrate the hot solution with 0·05 *N* potassium bromate solution.

Results

The method was devised for and applied to the analysis of the chlorostibinate of diphenylamine, $C_{12}H_{11}N.HSbCl_4$. This compound was prepared by Dr. F. G. Mann, F.R.S., of Cambridge University, by the action of antimony trichloride on diphenylamine.

The compound was found by the method of analysis described to contain 28·3 per cent. of antimony; the theoretical antimony content is 28·1 per cent. The complete analysis of the compound (average of duplicate determinations) was as follows—

	Analysis, %	Theoretical composition, %
Carbon (by micro-combustion)	33·3	33·2
Hydrogen (by micro-combustion)	2·9	2·8
Nitrogen (by micro-Dumas)	3·1	3·2
Chlorine (by micro-combustion)	33·0	32·7
Antimony (by the procedure described) ..	28·3	28·1
Total	100·6	100·0

The author wishes to thank Mr. A. C. Rolfe for helpful suggestions, and also Messrs. J. Alcock, F. R. Russell and J. Wrench for assistance with the experimental work.

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The Detection and Determination of Traces of Polynuclear Hydrocarbons in Industrial Effluents and Sewage*

By PHILIP WEDGWOOD and RONALD L. COOPER

A combination of chromatography and spectroscopy has been devised for the analysis of complex substances. It is particularly suited to the separation and identification of polynuclear hydrocarbons in gas-works and sewage effluents, and to the identification of traces of petroleum or tar oils.

In contrast to much of the previous work in this field, the method described gives rapid results, makes use of small alumina columns and detects trace quantities (0·001 to 0·1 mg) of several hydrocarbons in one sample.

In earlier work, Berenblum and Schoental[1] used a combination of chromatography and fluorescence spectrography to identify 3:4-benzpyrene in Scottish shale oil. A solution of 10 ml of the blue shale oil in a litre of light petroleum was passed through a large alumina column (20 × 6 cm) and the chromatogram was developed with petroleum, and then with increasing proportions of benzene, over a period of a week, 110 eluates of 200 to 500 ml each being collected and examined.

Winterstein and co-workers[2,3] demonstrated the order of adsorption on alumina of several polynuclear hydrocarbons by separating known compounds (40 to 200 mg of each) in pairs by elution with petroleum.

3:4-Benzpyrene, extracted from the tissue of a mouse treated with this hydrocarbon, has been estimated fluorimetrically after chromatography on silica gel by elution with petroleum and benzene (Weil-Malherbe[4]).

More recently, Kerne[5] has isolated 55 mg of chrysene from 3·5 kg of garden soil by chromatography of the benzene extract on a large alumina column (70 × 6·5 cm), and Neuworth[6] has attained a partial resolution of products from the hydrogenation of coal with light petroleum and a column of activated alumina plus Super-cel (50 × 4·8 cm).

The method as described below is part of an investigation into the nature of industrial effluents discharged to the sewers and their effect on the final sewage effluent.

Experimental

An extract in chloroform, or other suitable solvent, from which acidic and basic substances may or may not be removed, according to requirements, is carefully evaporated to dryness and the residue dissolved in *cyclo*hexane. The resultant solution is passed through a small alumina column (1·5 to 10 cm × 1 cm) and eluted with *cyclo*hexane. Absorption spectra of successive fractions of the eluate are measured by means of a Unicam SP500 spectrophotometer and compared with those of pure compounds.

Acids, phenols, bases and oxidised products of the hydrocarbons are held in the top of the alumina, whilst the hydrocarbons themselves pass down the column, separate from each other and then pass into the eluate. This separation of hydrocarbons from most of the interfering compounds facilitates their identification.

Artificial mixtures of known hydrocarbons have been treated in the same way and their order of adsorption agrees reasonably with the findings of Winterstein and co-workers.[2,3]

The order of adsorption of hydrocarbons from *cyclo*hexane solutions on to alumina appears to be as follows: naphthalene; acenaphthene; 9:10-dihydroanthracene; fluorene; phenanthrene; anthracene; pyrene; fluoranthene; 1:2-benzanthracene; chrysene; naphthacene and perylene; 3:4-benzpyrene and 1:12-benzperylene; anthanthrene; coronene.

Alkyl and aryl derivatives of the parent hydrocarbon appear to follow after the parent compound. For example, it has been found that anthracene is followed first by its 9-methyl derivative and then by its 9:10-dibenzyl derivative in a mixture of the three. Similarly, 3-methyl pyrene follows pyrene into the eluate.

* Part I of a series on Effluents.

Alumina of moderate activity is most suitable for the separation of hydrocarbons containing four rings. Pyrene, fluoranthene and 1:2-benzanthracene separate well. Chrysene and 1:2-benzanthracene are more difficult, but can be recognised spectroscopically when mixed together in an eluate. Naphthacene and the five- and six-ringed compounds usually require the addition of small amounts of benzene to the *cyclo*hexane when eluting. Anthraquinone, as an example of a simple oxidation product, does not interfere with these hydrocarbons, being held much more firmly in the column.

Method

Support, in a vertical position, a simple glass tube (25 × 1 cm) provided with a short compressed plug of glass wool at the bottom to support the column of alumina. Pour the alumina into the column as a thick slurry in the solvent to the required depth and lightly tap the column while the slurry is settling in order to even out the surface and give uniform density. The simple form of apparatus assists extrusion of the column, which, if desired, is carried out by removing the plug from the well-drained column, gently tapping the sides to allow the moist alumina to pass out slowly through the bottom and cutting the zones as they emerge.

Pass a concentrated solution of the extract in *cyclo*hexane through the column, develop the chromatogram with further *cyclo*hexane, and collect up to 100 fractions of eluate, if necessary, each about 3 ml in volume, for spectroscopic examination. Control development by studying the early fractions of the eluate, preferably by conducting a preliminary experiment.

During chromatography examine the eluates at a few specific wavelengths only, in order to identify the hydrocarbons by specific absorption peaks on the optical density scale.

Polynuclear hydrocarbons show highly characteristic spectra. As one passes from these to their alkyl substituted derivatives and then to their quinones and finally acidic and basic derivatives, the spectra become modified and less characteristic. Pyrene has an easily recognisable peak at 335 mμ and, if present, is a good indicator of column development. It should appear in about the tenth or twelfth fraction of eluate after about 20 minutes development for good separation of the four- to six-ringed compounds. In some instances the movement of coloured bands containing 3:4-benzpyrene is useful for following the separation.

Improved separation is effected by passing individual fractions of the eluate through fresh columns.

A list of the wavelengths, to the nearest mμ, of characteristic absorption peaks whereby some of the hydrocarbons are recognised is given in Table I.

Table I

Characteristic absorption peaks of some hydrocarbons

Hydrocarbon	Characteristic peaks: Best peaks, mμ	Characteristic peaks: Other useful peaks, mμ
Naphthalene	266, 276, 311	254, 297
Acenaphthene	289, 321	244, 279, 301, 306
9:10-Dihydroanthracene	263, 271	
Fluorene	301	262, 290
Phenanthrene	252, 293	275, 281
Anthracene	357, 376	252, 340
Pyrene	319, 335	273, 306
Fluoranthene	287, 359	276, 342
1:2-Benzanthracene	288	278
Chrysene	268	320
Naphthacene	441, 471	275
Perylene	436	409
3:4-Benzpyrene	365, 384, 403	297, 347
1:12-Benzperylene	302, 365, 384	347
Anthanthrene	423, 430	407
Coronene	302, 339	

Relative height and shape of the peaks, their relative rate of rise and fall, chromatographic sequence and position must all be taken into account. It will be noticed that 3:4-benzpyrene

and 1:12-benzperylene have similar absorption curves, but they can be distinguished in the following three ways: (*a*) 3:4-benzpyrene has a peak at 297 mμ, whereas 1:12-benzperylene has a sharper corresponding peak at 302 mμ, (*b*) the 3:4-benzpyrene peak has a distinct shoulder at 380 mμ, which is not shown in the absorption spectrum of the other

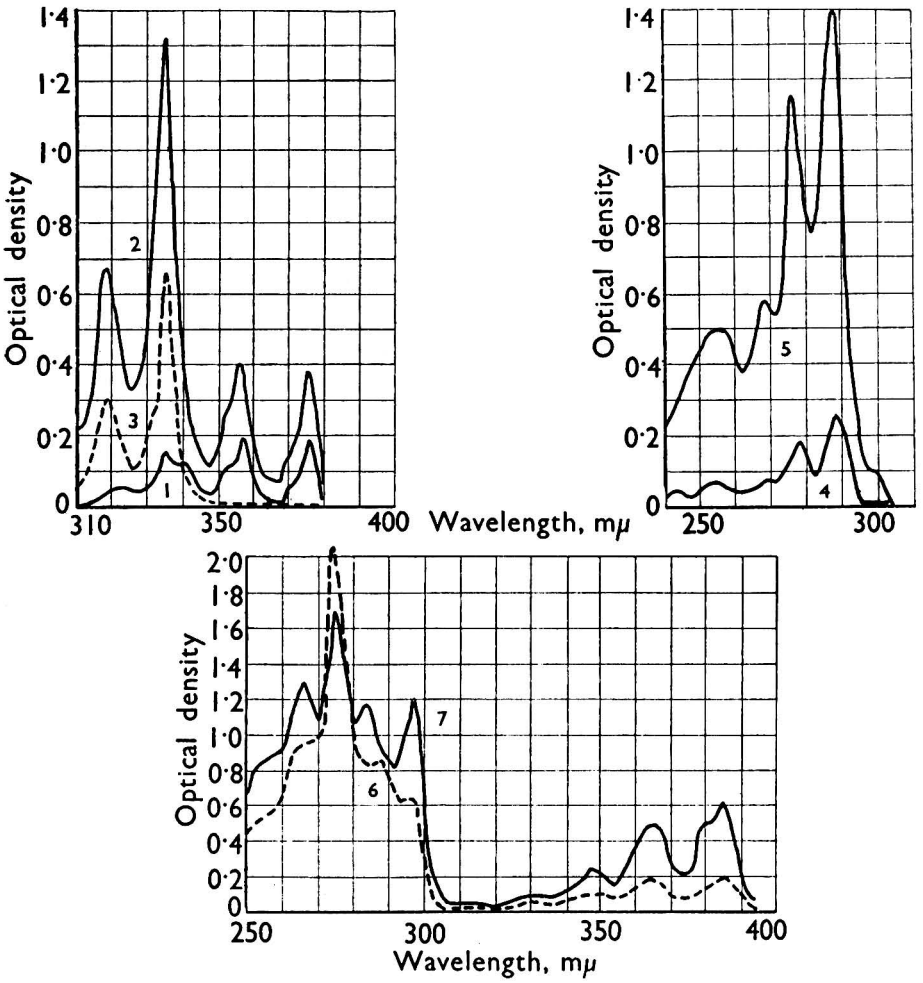

Fig. 1. Separation of a mixture of anthracene, pyrene, 1:2-benzanthracene, naphthacene and 3:4-benzpyrene in *cyclo*hexane.

Eluate fraction	Hydrocarbons present
1	Anthracene + trace of pyrene
2	Anthracene + pyrene
3	Pyrene
4, 5	1:2-Benzanthracene
6	Naphthacene + trace of 3:4-benzpyrene
7	Less naphthacene + more 3:4-benzpyrene

hydrocarbon, and (*c*) 1:12-benzperylene has only a low peak above 400 mμ, which would not be detected at the concentrations used in this type of qualitative analysis.

Generally speaking, absorption peaks at the higher wavelengths are more characteristic of a particular hydrocarbon than those below 300 mμ and, further, they stand out more clearly from background absorption. For example, pyrene and 3-methyl pyrene are difficult to distinguish below 300 mμ, but are readily differentiated by their last big absorption peaks, as in the parent compound this is at 335 mμ, whilst in the derivative it is 344 mμ.

For the study of absorption spectra below 280 mμ, spectroscopically pure *cyclo*hexane must be used. Above this wavelength, benzene may be permitted in the *cyclo*hexane in small proportions. Above 310 mμ, pure benzene is satisfactory.

Separation of artificial mixtures

The following examples illustrate the method and show how the hydrocarbons can be recognised even with relatively poor separations.

A mixture of anthracene, pyrene, 1:2-benzanthracene, naphthacene and 3:4 benzpyrene in *cyclo*hexane separated in the order given, when passed through a weakly active column of alumina, in only seven fractions of eluate, as shown in Fig. 1.

Fig. 2 shows an important and interesting separation of four compounds, illustrating how effectively the method separates hydrocarbons from their oxidation products. A mixture of anthracene, 3:4-benzpyrene, anthraquinone and phenol separated easily in the order given. The anthraquinone required a considerable proportion of benzene in the *cyclo*hexane to bring it into the eluate, and chloroform was necessary to elute the phenol. Aniline,

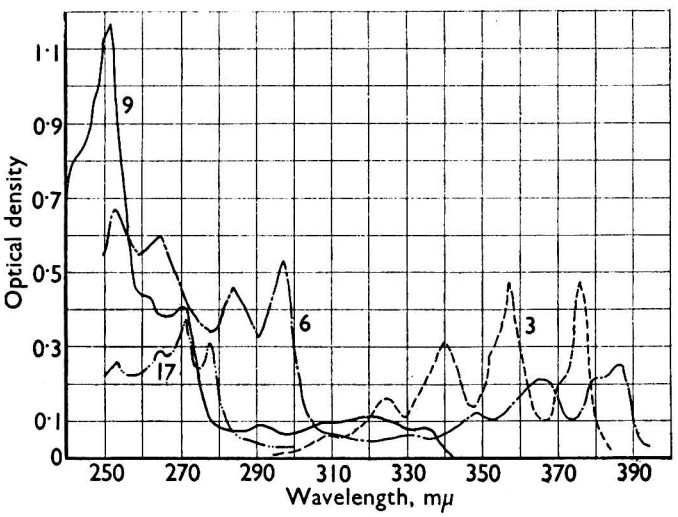

Fig. 2. Separation of hydrocarbons from their oxidation products. Fraction 3, anthracene; fraction 6, 3:4-benzpyrene; fraction 9, anthraquinone; fraction 17, phenol

similarly, is very strongly held by alumina. It can be seen that, provided organic acids and bases are not present in great excess, acid or alkali extraction is not necessary before chromatography. The method is therefore useful for examining traces of oil when only a milligram or less is available for analysis.

Application to industrial analytical problems

A considerable amount of work has been carried out on a range of complex materials and the method found to be very effective. Some of this work will be described in subsequent papers.

The authors thank Imperial Chemical Industries Limited and Professor J. W. Cook, F.R.S., for gifts of some of the hydrocarbons used in the investigation.

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The Use of Inorganic Complexes in Colour Reactions for Organic Compounds

Part I. The Determination of *iso*Nicotinic Acid

By E. F. G. HERINGTON

The quantitative determination of *iso*nicotinic acid in the presence of nicotinic and dipicolinic acids by means of an aqueous solution of tri-sodium pentacyanoamminoferrate, glycerol and acetic acid is described. The results of the analyses of synthetic mixtures are presented, and it is shown that picolinic acid does not interfere with the determination.

THE use of organic co-ordinating compounds for the colorimetric, gravimetric or volumetric determination of inorganic anions and cations is now widely practised, but the use of inorganic complexes as colorimetric reagents in organic chemistry is less common. This paper describes the use of tri-sodium pentacyanoamminoferrate, together with suitable additives, for the colorimetric determination of *iso*nicotinic acid. The use of *iso*nicotinic acid hydrazide for the treatment of tuberculosis makes the determination of the parent acid of this compound of some interest. One method of preparing *iso*nicotinic acid is by oxidising γ-picoline obtained from coal tar; this pyridine base occurs together with β-picoline and 2:6-lutidine in the close-boiling commercially available "β-picoline" fraction, so that incomplete separation of these bases would lead to contamination of the *iso*nicotinic acid by nicotinic and dipicolinic acids. The rapid colorimetric method of analysis here described permits the estimation of *iso*nicotinic acid in samples of mixed pyridine carboxylic acids containing nicotinic, picolinic and dipicolinic acids. The method has not been tried for the estimation of this acid in biological fluids.

The nomenclature advocated by a Committee of the International Union of Chemistry in 1940[1] has been adopted in the present paper, so that the salt $Na_3[Fe(CN)_5NH_3]$, which is prepared by the action of concentrated ammonium hydroxide on sodium nitroprusside, is called tri-sodium pentacyanoamminoferrate, and the salt $Na_2[Fe(CN)_5NH_3]$, which is made from the tri-sodium compound by oxidation, is called di-sodium pentacyanoamminoferrate. The ion $[Fe^{II}(CN)_5NH_3]'''$ moderately readily undergoes oxidation in aqueous solution in the presence of air to the ion $[Fe^{III}(CN)_5NH_3]''$, and frequently no distinction has been made between the action of these two ions in colour reactions described in the literature. The ion $[Fe^{II}(CN)_5NH_3]'''$ is, however, responsible for the red colour produced by *iso*nicotinic acid in the present experiments, as it has been shown that this pyridine carboxylic acid does not produce a red colour with $Na_2[Fe(CN)_5NH_3]$ under the conditions of the analysis.

The use of the salt $Na_3[Fe(CN)_5NH_3]$ in certain organic colour reactions has previously been recorded. Baudisch[2] has described the violet colour formed by nitrosobenzene with the complex salt and the inhibition of the formation of this colour by pyridine. Schwechten[3] has reported that the complex gives colours with certain thiocarbonyl compounds and also with some aldehydes in the presence of hydrogen sulphide. Feigl[3,4,5,6,7] has discussed the colours produced by nitroso-compounds and by thioaldehydes, thioketones and hydrazines with this salt, and Fearon[8] has recorded the use of a partly oxidised solution of the complex in tests for guanidines, urea and thiourea. Most of these reactions have been advanced as qualitative tests, but more recently a paper describing the quantitative determination of Propamidine and M & B 1270 by tri-sodium pentacyanoamminoferrate has been published (Trought, Ashton and Baker[9]).

The reagent solution used in the method described is green, whereas *iso*nicotinic acid produces a reddish colour, and hence it is necessary to use a photo-electric absorptiometer with suitable filters to measure the depth of colour. A Spekker absorptiometer with Ilford No. 604 filters is used. This colour reaction is sensitive to hydrogen-ion concentration and is therefore carried out in the presence of a large controlled excess of acetic acid. Glycerol is added to the reagent both to intensify the colour and to keep the complexes in solution. The aqueous tri-sodium pentacyanoamminoferrate solution deteriorates moderately rapidly on keeping

and therefore this solution should be made up immediately before use. In agreement with the observations of Fearon[8] it was established that the solid complex keeps well in a desiccator over calcium chloride in the dark.

PREPARATION OF $Na_3[Fe(CN)_5NH_3].H_2O$—

The preparation of this material has been described by Hofmann[10] and more recently by Fearon[8], but the following conditions were found suitable in the present work.

Weigh out 10 g of finely ground sodium nitroprusside into a small conical flask and add 24 ml of ammonium hydroxide, sp.gr. 0·880. Shake well and loosen the cork so that gas can escape; when all the solid has dissolved and gas evolution has begun, place the flask in a refrigerator at −7° C for 48 hours. Warm to room temperature, add a little more ammonium hydroxide, sp.gr. 0·880, filter with the aid of a filter-pump, remove as much liquor as possible and then wash the precipitate with a small amount of methyl alcohol. Quickly remove as much of this alcohol as possible by suction, transfer the product to a glass dish in a desiccator over anhydrous calcium chloride and keep it in the dark.

A typical preparation by this method yielded 5·4 g. A further quantity of the complex, but of a lower grade, can be prepared by adding ethyl alcohol to the filtrate; although this material can be used in the test, it is not recommended and it was not used in the present work.

PURITY OF PYRIDINE CARBOXYLIC ACIDS USED—

The acid samples, which were kept in a desiccator over phosphorus pentoxide, had been prepared by oxidising samples of the appropriate picoline and lutidine homologues, which were at least 99·7 moles per cent. pure.

METHOD FOR THE QUANTITATIVE DETERMINATION OF *iso*NICOTINIC ACID

REAGENTS—

Acetic acid, diluted—Dilute 100 ml of glacial acetic acid with 400 ml of distilled water.

Aqueous glycerol—Dilute 10 ml of pure glycerol with 20 ml of distilled water.

Tri-sodium pentacyanoamminoferrate solution—Dissolve 0·1 g of tri-sodium pentacyanoamminoferrate in 20 ml of distilled water immediately before use.

PROCEDURE—

Wash about 0·05 g of pure *iso*nicotinic acid, accurately weighed, into a 100-ml calibrated flask with diluted acetic acid reagent and make up to the mark with the reagent. Treat a 0·05-g sample, accurately weighed, of the unknown pyridine carboxylic acid similarly.

Place 2·0 ml of the pure *iso*nicotinic acid solution in a clean dry boiling-tube (tube 1), and place 2·0 ml of the dilute acetic acid solution of the unknown pyridine carboxylic acid in a second tube (tube 2). Place 2·0 ml of diluted acetic acid reagent in a third tube (tube 3). To each tube add 2·5 ml of aqueous glycerol and shake the tubes. To each tube then add 2·5 ml of freshly prepared tri-sodium pentacyanoamminoferrate solution, shake the tubes, and set them aside at room temperature (approximately 20° C) for 15 minutes.

Set the Spekker absorptiometer drum to 1·00, using Ilford No. 604 filters, with a 1-cm cell filled with the solution from tube 3 in the light path. Immediately record the light absorption with the 1-cm cell filled with the solutions from tubes 1 and 2. Let these drum readings be x and y, respectively. Calculate the weight percentage of *iso*nicotinic acid from the expression $100(1{\cdot}00 - y)/(1{\cdot}00 - x)$.

RESULTS

Results of determinations by this method of *iso*nicotinic acid in synthetic mixtures are summarised in Table I, which shows a maximum error of 4 per cent. when the *iso*nicotinic acid content lies in the range 10 to 100 per cent.

Nicotinic acid does not give a red colour in this test, but it was observed that with the reagent it gives a slightly more transparent solution than the reagent itself. Thus the Spekker absorptiometer drum reading for a 2·0-ml portion of a nicotinic acid solution (0·05 g in 100 ml of diluted acetic acid) with the reagent was found to be 1·03 when the drum had been set to 1·00 with reagent alone, *i.e.*, this solution had an apparent *negative* concentration of 4 per

cent. of *iso*nicotinic acid, as the reading x was equal to 0·20 with the present equipment. Clearly the method is not well suited to the determination of the *iso*nicotinic acid content of mixtures of pyridine carboxylic acids weak in *iso*nicotinic acid (*i.e.*, when the *iso*nicotinic acid content is less than 10 per cent.).

*iso*Nicotinic acid samples prepared by oxidation of the appropriate "β-picoline" fraction may contain some picolinic acid derived from α-ethyl pyridine because the boiling point of this base is near that of γ-picoline; however, picolinic acid does not interfere with the

TABLE I

DETERMINATION OF *iso*NICOTINIC ACID IN MIXTURES OF *iso*NICOTINIC, NICOTINIC AND DIPICOLINIC ACIDS

Synthetic mixture			
Nicotinic acid, % w/w	Dipicolinic acid, % w/w	*iso*Nicotinic acid, % w/w	*iso*Nicotinic acid found, % w/w
10	—	90	89
—	10	90	92
10	10	80	78
25	—	75	75
—	25	75	79
50	—	50	51
25	25	50	53
—	50	50	54
33·3	33·3	33·3	34
80	—	20	17
40	40	20	19
—	80	20	20
90	—	10	6
—	90	10	10

estimation of *iso*nicotinic acid. For example, an *iso*nicotinic acid content of 53 per cent. was found for a synthetic mixture of 50 per cent. of *iso*nicotinic acid and 50 per cent. of picolinic acid

The pyridine carboxylic acids are amphoteric electrolytes, and occasionally solid samples may be contaminated with strong electrolytes, *e.g.*, sulphuric acid or sodium hydroxide, but experiment showed that solutions containing up to at least one equivalent of strong inorganic acid or base gave colours of the same intensity as solutions of equal *iso*nicotinic content in the absence of extra electrolyte. The method can therefore be used under these conditions.

I wish to thank Dr. R. F. Evans for making and supplying the pyridine carboxylic acids used. The work described has been carried out as part of the research programme of the Chemical Research Board, and this paper is published by permission of the Director, Chemical Research Laboratory, Teddington.

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The Determination of Ammonia in the Presence of Hydrazine

By W. PUGH and (the late) W. K. HEYNS

Procedures are described for the determination of ammonia in mixtures of ammonium and hydrazine salts. They involve, as a preliminary to the distillation of ammonia, the oxidation of hydrazine with iodic acid, bromine or alkaline permanganate. The effectiveness of all three oxidants and the speed, simplicity and accuracy of the method are indicated.

In the course of preparing some new hydrazine compounds in this laboratory, the need arose for estimating the extent to which they were contaminated with ammonium salts that might have been produced by catalytic decomposition or by autoxidation of hydrazine.[1] Owing to the volatility of hydrazine and to the ease with which it is oxidised by air,[2] it was assumed at the outset that the conventional distillation method would give erratic results for ammonia, and a few preliminary distillations of mixtures of ammonium and hydrazine salts confirmed this.

A search of the literature revealed that whilst methods for determining hydrazine in presence of ammonium salts abound,[3] no tests have been made to find the best means of eliminating the effects of hydrazine in the estimation of ammonia. Several workers,[4,5,6,7] who have investigated the oxidation of hydrazine and its salts, have found that ammonia is frequently one of the products, and they have assumed, for the purpose of estimating the ammonia by the usual distillation method, that no other interfering products are formed. This may be a justifiable assumption, but it seemed desirable to test it and to find, at the same time, the most suitable oxidants for destroying hydrazine before distilling the ammonia.

Reagents that oxidise hydrazine partly to ammonia include chlorates,[5] bromates,[5] hydrogen peroxide,[6] persulphates,[6] acid permanganate,[6,7,8] manganese and lead dioxides,[6] manganic salts[9] and ferric salts.[10] On the other hand, reagents that are reported to oxidise hydrazine quantitatively to nitrogen, and which alone would serve the purpose of this investigation, include iodic acid,[3,5,11,12] bromine,[3] alkaline permanganate,[12,13] iodine,[3,12] hypochlorous acid[3] and ferricyanides.[14] Of these, the first three were selected for investigation, as they would be the most suitable if applicable. All three were found to oxidise hydrazine smoothly and rapidly and to allow subsequently the accurate distillation of ammonia.

In testing these oxidants hydrazine monohydrochloride, made by adding the calculated amount of hydrazine dihydrochloride to hydrazine hydrate (50 per cent.), precipitating with 4 volumes of methanol and recrystallising from 80 per cent. methanol, was used. The product was analytically pure within the limits of experimental error. Analytical reagent quality ammonium sulphate, ammonium chloride and ammonium nitrate were dried at 100° C before use. The oxidants were all laboratory chemicals of good quality.

The general procedure was to add known weights of hydrazine hydrochloride to known volumes of the standard ammonium salt solutions and, after oxidation as described specifically below for each oxidant, to distil the ammonia. Semi-micro amounts were used in a distillation apparatus similar to the one described by Ma and Zuazaga.[15] Boric acid was used as absorbent in conjunction with bromocresol green - methyl red mixed indicator.

Method

Oxidation procedures—

With iodic acid—Treat the sample with sufficient hydrochloric acid to bring the acidity to approximately 3·5 *N* and then add potassium iodate until the colour of the iodine liberated is discharged. Add sufficient stannous chloride to decolorise the iodine liberated by reduction of the iodine monochloride, and transfer to the distillation apparatus.

With bromine—Acidify the sample, if not acidic already, and add sufficient bromine or bromine water to impart a distinct colour to the solution. Boil off the excess of bromine or add a small excess of stannous chloride. The solution is then ready for distillation.

With alkaline permanganate—Place the sample directly in the distillation apparatus, wash it in completely, add sufficient alkali for the distillation and then, immediately afterwards, an excess of permanganate solution. Distillation can then be started without delay, as oxidation by the permanganate is rapid. NOTE—It is important to adhere to this order of mixing. High results were always obtained when the permanganate solution was added before the alkali.

RESULTS

TABLE I

EFFECT OF OXIDANT ON DETERMINATION OF AMMONIA CONTAINING HYDRAZINE

20·00 ml ammonium sulphate solution containing 1·503 g per litre taken

Hydrochloric acid concentration = 0·02176 *N*

Theoretical titre = 20·92 ml of hydrochloric acid

Procedure	Distillation time, minutes	Hydrazine hydrochloride added, g	Oxidant added, g	Hydrochloric acid titre, ml
Iodic acid	10	0·00	0·1	21·00
	10	0·00	0·2	20·98
	10	0·04	0·15	20·92
	10	0·04	0·2	20·94
	8	0·04	0·18	20·80
	10	0·10	0·4	20·95
	10	0·20	1·0	20·92
	9	0·30	1·5	20·90
	12	0·40	2·0	20·93
	15	0·55	2·0	21·08
Bromine	9	0·00	Excess	20·91
	9	0·05	,,	20·95
	10	0·05	,,	20·93
	11	0·05	,,	20·97
	9	0·10	,,	21·02
	12	0·15	,,	21·06
Alkaline permanganate	10	0·00	0·2	20·90
	10	0·05	0·2	20·90
	10	0·05	0·3	21·00
	10	0·04	0·2	21·00
	10	0·14	0·3	21·00
	10	0·17	0·4	20·95
	15	0·42	1·0	21·08
	12	0·12	0·3	21·06
	6	0·10	0·2	18·0

Table I shows that equally good results are given by all three procedures. The variations, which are small and irregular, are due chiefly to the difficulty in locating the end-point with such dilute solutions and possibly to variable but small amounts of ammonia in the distilled water. The tendency to high results after longer distillation was definitely linked with the end-point difficulty at the greater dilutions. For the quantities handled a distillation time of 9 to 10 minutes is necessary and sufficient. Of the three, the bromine and the permanganate methods are the most convenient. Ammonium chloride and ammonium nitrate solutions gave similar results.

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CHEMISTRY DEPARTMENT
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June 30th, 1952

Notes

THE DETERMINATION OF MAGNESIUM IN PLANT MATERIAL BY MEANS OF ETHYLENEDIAMINE-TETRA-ACETIC ACID

IN pot experiments designed for studying the effects on the growth of plants of applications of copper to the soil, it was found that acid digests of the roots frequently contained little magnesium, but much copper, iron and manganese. The usual methods for determining magnesium are not applicable to these solutions. A method is described here for determining magnesium by titration with ethylenediamine-tetra-acetic acid (EDTA), after prior separation of interfering metals. Diehl's method[1] is used for the EDTA titration, except that the di-sodium salt of EDTA is replaced by a solution of the ammonium salt, which has been found to give a better end-point.

METHOD

REAGENTS—

8-Hydroxyquinoline solution—Add 2 g of 8-hydroxyquinoline to 100 ml of boiling 4 per cent. acetic acid solution and stir rapidly until dissolved. For digests of plant tops containing relatively small amounts of interfering metals, prepare, similarly, a 1 per cent. oxine solution.

Ammonium hydroxide, 5 N.

Carbon tetrachloride, B.P.

Sodium diethyldithiocarbamate solution—A 1 per cent. w/v aqueous solution, prepared just before use.

Ammonium oxalate—A saturated solution.

Nitric acid—Analytical reagent grade, sp.gr. 1·42.

Ammonium hydroxide - ammonium chloride buffer solution—Dissolve 27 g of analytical grade ammonium chloride and 228 ml of ammonium hydroxide, sp.gr. 0·880, in water and dilute to 400 ml.

Indicator A—Mix 2·25 g of hydroxylamine hydrochloride with 0·25 g of Eriochrome Black T, dissolve in 50 ml of absolute alcohol and filter.

Indicator B—Mix 2·25 g of sodium diethyldithiocarbamate with 0·25 g of Eriochrome Black T, dissolve in 50 ml of absolute alcohol and filter. Prepare immediately before use.

Standard magnesium solution—Dissolve 1·2670 g of magnesium sulphate, $MgSO_4.7H_2O$, in water and dilute to 500 ml; 1 ml contains 0·25 mg of magnesium.

EDTA solution—Suspend 3·14 g of EDTA in about 500 ml of water and titrate with 5 *N* ammonium hydroxide to a pH of 10·0, using a glass electrode. Filter through a Whatman No. 41 filter-paper and dilute to 1 litre; 1 ml ≡ approximately 0·25 mg of magnesium.

PROCEDURE—

To an aliquot of the nitric - perchloric acid digest solution add 10 ml of hydroxyquinoline solution and titrate with 5 *N* ammonium hydroxide to a pH of 5·25, using the glass electrode. Bring nearly to the boil and filter hot through a Whatman No. 42 filter-paper into a 125-ml pear-shaped Pyrex-glass separating funnel. When cool, shake twice with 5 to 10-ml portions of carbon tetrachloride. Add 5 ml of diethyldithiocarbamate solution and extract the purple manganese complex by shaking for 2 minutes with 5 to 10 ml of carbon tetrachloride. Five minutes should be allowed to elapse between addition of reagent and extraction. Add a further 1 ml of diethyldithiocarbamate and shake for 1 minute with carbon tetrachloride to ensure that all the manganese has been extracted. Run the aqueous phase into a 250-ml squat beaker and boil to expel the solvent. To the solution, maintained at about 90° C, add 5 ml of ammonium oxalate solution, stir well, and leave for 5 to 10 minutes on a hot-plate until the precipitate settles. Set aside

overnight at room temperature, then filter off the calcium oxalate with the aid of a filter-stick, and dilute the filtrate to 100 ml.

Transfer an aliquot of the filtrate (not exceeding 25 ml) to a 100-ml Pyrex-glass conical flask, dilute to approximately 50 ml, and add successively 1 ml of buffer solution, 4 drops of indicator B and 4 drops of indicator A, swirling after each addition. Titrate with EDTA until a blue colour appears, add 0·5 ml of EDTA in excess, then after 1 minute titrate the excess of EDTA with standard magnesium solution. With this technique, 5 mg of phosphorus do not affect the accuracy of the titration. A titre of at least 2 ml of EDTA (0·5 mg of magnesium) is desirable.

RESULTS—

In aliquots larger than 25 ml, acetate and oxalate interfere. Digestion of the aliquot with 25 ml of nitric acid reduces, but does not eliminate, this interference. Nitric acid digestion was used in the experiments the results of which are shown in Table I, the entire calcium filtrate being taken. Charring must be avoided in the final stages of the digestion by carefully regulating the heat applied; the residue must be white.

TABLE I

RECOVERIES OF MAGNESIUM BY THE PROPOSED METHOD

Composition of nitric acid digest				
Magnesium, mg	Calcium, mg	Phosphorus, mg	Iron, aluminium, copper and manganese, mg	Magnesium recovered, %
1·25	0	0	0	97·8
1·25	5	0	0	97·8
1·25	5	5	0	98·4
1·25	0	0	5 (of each)	97·7
1·25	5	0	5 (")	98·1
1·25	0	5	5 (")	98·4
1·25	5	5	5 (")	97·6
			Mean recovery	98·0

Experimental results showed that most of the apparent loss of magnesium could be accounted for by retention of magnesium by the filter-paper in the filtration of the quinolates.

Recoveries of magnesium added to digests of roots containing about 0·5 per cent. of magnesium oxide, 1000 μg of iron per g and 50, 880 or 890 μg of copper per g were 99·0, 100·8 and 98·6 per cent., respectively.

In digests containing little magnesium, it may be possible to overcome acetate and oxalate interference by titrating an aliquot of the calcium filtrate with a more dilute solution of EDTA than that used above, instead of digesting the entire aliquot with nitric acid. Debney's method[2] of using 0·0005 *M* EDTA solution to titrate as little as 12 $\pm$ 4 μg of magnesium may be useful in this connection.

Thanks are due to Dr. D. J. D. Nicholas for his advice throughout these experiments.

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July 17th, 1952

TITRIMETRIC DETERMINATION OF SODIUM IN BIOLOGICAL FLUIDS

IN my method for the rapid determination of sodium in serum,[1] a colorimetric finish was used. Further work has shown that it is possible to apply a titrimetric finish by using a modification of the method of Cooke, Hazel and McNabb,[2] in which chromous chloride is used to reduce uranium^{VI} to uranium^{IV} in aqueous solution, the excess of chromous chloride being removed by atmospheric

oxidation. The low-potential redox dye phenosafranine is used to indicate when oxidation is complete. The uranium^{IV} is then titrated with standard dichromate in the presence of ferric alum and phosphoric acid. The method is unsuitable in the presence of alcohol, which has a tendency to be oxidised by the dichromate. Ceric ammonium sulphate was substituted for dichromate with entirely satisfactory results; this oxidising agent also has the advantage that it does not require phosphoric acid to be added to the solution before titration. Other modifications of the method of Cooke, Hazel and McNabb include a more convenient method for preparing the zinc amalgam and the use of neutral red in place of phenosafranine, which gives a less satisfactory colour change on re-oxidising the chromous chloride.

Method

Apparatus—

Glassware and pipettes—As for the colorimetric method.[1] For consistent results all pipettes should be calibrated before use.

Reagents—

All reagents should be of recognised analytical purity.

Sodium reagent—The alcoholic magnesium uranyl acetate solution used for the colorimetric method.[1]

Zinc amalgam—Place 12 g of zinc powder in a 100-ml glass-stoppered separating funnel. Add 50 ml of mercury and 5 ml of 4 *N* sulphuric acid. Shake the mixture until all the zinc has dissolved in the mercury (after about 2 minutes). Transfer the lower layer of zinc amalgam to a 100-ml glass-stoppered bottle containing 5 ml of *N* sulphuric acid.

Chrome alum reagent, 0·5 N—Dissolve 125 g of chrome alum, $KCr(SO_4)_2.12H_2O$, in sufficient 2 *N* hydrochloric acid to make 500 ml of solution.

Chromous chloride, 0·5 N—Place 10 ml of zinc amalgam, 25 ml of 0·5 *N* chrome alum reagent and 15 ml of light petroleum in a 50-ml glass-stoppered bottle. Shake the mixture vigorously until the middle layer of liquid is bright blue (after about 2 minutes). The chromous chloride can be stored in a refrigerator for long periods, but the solution will need to be regenerated occasionally by vigorous shaking.

Sulphuric acid - neutral red solution—Mix 20 ml of concentrated sulphuric acid with 1 litre of water and add 10 ml of a 0·05 per cent. aqueous solution of neutral red.

Indicator solution—Dissolve 100 mg of barium diphenylamine sulphonate in sufficient warm water to make 100 ml of solution.

Ceric ammonium sulphate, 0·01 N—Dilute 200 ml of a stock 0·05 *N* solution of ceric ammonium sulphate with sufficient *N* sulphuric acid to make 1 litre of solution. Standardise the 0·01 *N* solution at monthly intervals against freshly prepared 0·01 *N* arsenious oxide, using 0·1 ml of 0·0005 *M* *o*-phenanthroline ferrous sulphate as indicator and 0·1 ml of 0·1 per cent. osmic acid as catalyst for 20 ml of solution.

Ferric alum solution, 5 per cent.—Dissolve 50 g of ferric ammonium sulphate, $FeNH_4(SO_4)_2.12H_2O$, in sufficient *N* sulphuric acid to make 1 litre of solution. Clarify the cloudy liquid by filtration.

Procedure—

Initially this is the same as for the colorimetric method.[1] After centrifuging, transfer 4 ml of the supernatant fluid from each tube to 100-ml conical flasks. Add 10 ml of sulphuric acid - neutral red solution to each flask. Add 0·5 *N* chromous chloride drop by drop until the liquid in each flask changes in colour from pink through slate blue to apple green. From then on treat each flask individually. Swirl the contents of one flask until the slate-blue colour reappears. Add 1 ml of 5 per cent. ferric alum solution and 0·5 ml of indicator solution. Titrate the mixture with 0·01 *N* ceric ammonium sulphate solution. The end-point is near when the liquid in the flask turns a greyish colour. Then add the ceric ammonium sulphate drop by drop until a deep purple colour appears. This is the end-point. Swirl the contents of the second flask until the slate blue colour reappears. Titrate with 0·01 *N* ceric ammonium sulphate solution after the addition of ferric alum and indicator solutions.

$$\text{Serum sodium} = 48{\cdot}88\ (x - y)\ \text{mg per ml},$$

where x ml is the amount of 0·01 *N* ceric ammonium sulphate required for blank and y ml is the amount required for test.

The figure 48·88 is the theoretical factor, assuming Na ≡ 3U ≡ 6H.

Results

To test for the effect of possible interfering substances, the following experiments were performed. An aqueous solution was prepared, containing 0·8 g of uranium acetate, 3 g of magnesium acetate and 3 ml of glacial acetic acid per 100 ml of solution. Five different serum or plasma samples and two urine samples, each 0·1 ml, were added to 5-ml amounts of 80 per cent. v/v alcohol. The mixtures were centrifuged and 4-ml portions of the supernatant fluids were transferred to a series of conical flasks. To one of the flasks containing serum extract, 1 mg of glucose and 1 mg of urea were added; to one of the flasks containing urine extract, 10 mg of glucose and 10 mg of urea were added. Four millilitres of the 0·8 per cent. w/v aqueous uranium solution were added to each of the seven flasks and to another conical flask containing 4 ml of water. Ten millilitres of sulphuric acid - neutral red solution were added to each flask. The mixtures were reduced and titrated according to the method proposed. The results are shown in Table I.

Table I

Effect of alcoholic extracts of serum, plasma or urine on 4 ml of 0·8 per cent. aqueous uranium acetate solution

Extract	Amount of 0·01 *N* ceric ammonium sulphate used, ml	Extract	Amount of 0·01 *N* ceric ammonium sulphate used, ml
Blank	15·45	Plasma 1	15·45
Serum 1	15·45	Serum 4 + 1 mg of glucose + 1 mg of urea	15·45
Serum 2	15·4	Urine 1	15·65
Serum 3	15·45	Urine 1 + 10 mg of glucose + 10 mg of urea	15·65

These results show that with serum there is no interference, even when glucose and urea are present simultaneously in amounts equivalent to 1000 mg per 100 ml of serum. With urine there is some interference, although this is not due to the presence of either urea or glucose, which may be present simultaneously in amounts equivalent to 10 g per 100 ml of urine without causing interference.

Standard solutions of sodium chloride gave the results shown in Table II. The method appears to be unreliable when the sodium concentration exceeds 400 mg per 100 ml.

Table II

Analysis of standard sodium chloride solutions by the proposed method

Sodium present, mg per 100 ml	Sodium found, mg per 100 ml					
100	103,	100,	100,	103,	103,	98
200	202,	201,	201,	203,	201,	200
300	305,	298,	296,	304,	304,	299
350	352,	348,	350,	350,	352,	348
400	394,	399,	402,	397,	406,	396
500	489,	487,	480,	502	—	—

Ten serum samples analysed according to the proposed method and a gravimetric method[3] gave the results shown in Table III.

Table III

Determination of sodium in serum by the proposed method and by a gravimetric method

Sample No.	1	2	3	4	5	6	7	8	9	10
Sodium by gravimetric method, mg per 100 ml	332	328	324	329	331	325	322	316	281	322
Sodium by proposed method, mg per 100 ml	335	319	328	330	335	325	328	313	284	320

The method can be applied directly to cerebrospinal fluid, serum or plasma (Wintrobe's anti-coagulant). For urine, 250 mg of solid calcium hydroxide are added to 5 ml of urine contained in a glass-stoppered centrifuge tube. The tube is stoppered and shaken vigorously for 1 minute.

After centrifugation, the clear phosphate-free supernatant fluid is used for analysis. Since urine interferes slightly with the titration, 0·08 ml of the phosphate-free urine is added to the blank just before the chromous chloride is added, so that any increase in the test titration will be counterbalanced by a similar increase in the blank titration.

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August 1st, 1952

THE DETERMINATION OF SMALL QUANTITIES OF BORON

THE problem arose of determining the amount of boric acid in fragments of wood, each weighing not more than 50 mg and containing from 0 to 100 μg of boric acid (0 to 17 μg of boron).

It was originally proposed to use the fluorimetric method,[1] which has the advantage of giving a linear relationship between the intensity of fluorescence and the concentration of boron solution for a wide range of boron concentrations. The boric acid was to be recovered from the wood by prolonged steeping in water. This recovery technique is obviously of limited applicability, and the probability of having to separate boron by methyl borate distillation is also a drawback in this method. As it happened, the only fluorimeter available was found unsuitable for measuring the weak fluorescence of the reaction mixture, in which 1 ml of aqueous boron solution is diluted to 50 ml with alcohol, so the method was abandoned.

The Chromotrope B colorimetric method[2] was next applied. Transmittances were compared in a Beckman spectrophotometer. Despite many variations in the method of preparing the reaction mixture, standard curves were never smooth and reproducible, and this method was discarded in favour of the well-tried quinalizarin method.

In the standard procedure,[3] approximately 0·05 mg of quinalizarin is present in 10 ml of the reaction mixture. If we assume the equilibrium reaction to be—

$$\text{Quinalizarin} + 2H_3BO_3 \rightleftharpoons \text{Quinalizarin},\ 2H_3BO_3,$$

then the greatest amount of boric acid (M.W. = 61·8) that can react with 0·05 mg of quinalizarin (M.W. = 272) is about 23 μg. Since the reaction does not proceed to completion, the limiting amount of boric acid that can be determined is slightly greater, about 30 μg. Nevertheless, when the amount of boric acid exceeds 20 to 25 μg, sensitivity is poor.[3,4]

An increase in the concentration of quinalizarin reagent in the reaction mixture aids complex formation at any boric acid concentration; the measurable range of this acid concentration will also be increased. Although the resulting colours cannot be compared visually, the transmittances of light of a narrow waveband can be measured in a spectrophotometer, or any other type of photometer equipped with a selective filter. On account of increased complex formation, a spreading of these transmittances is to be expected with an increasing amount of reagent, with consequent gain in sensitivity. This is borne out by the slopes of the curves A to E shown in Fig. 1, which were obtained by the following procedure.

To 1 ml of boric acid solution were added y ml of 99·2 per cent. sulphuric acid (analytical reagent grade). After the mixture had been cooled, x ml of 0·01 per cent. w/v quinalizarin in 99·2 per cent. sulphuric acid were added; the final volume ($1 + x + y$) equalled 11·5 ml. The usual precautions were taken of guarding the strong acids from atmospheric moisture. After setting aside overnight, transmittances were compared in 1-cm glass cuvettes, in a Beckman D.U. spectrophotometer, against a reference standard similarly prepared with 1 ml of water. The nominal wavelength was 620 mμ, slit-width 1 mm, and spectral band width 38 mμ.

The maximum amount of reagent that can be advantageously used is determined by the increasing loss of instrument response or sensitivity with increasing intensity of colour. An excellent compromise was reached by working on a curve lying between B and C (Fig. 1). This was F, in which $y = 8$ and $x = 2$.

Transmittance values can be slightly further spread by using narrower slit-widths, but this too is undesirable on account of the loss of instrumental response.

Curve A was given by the conventional quinalizarin procedure. As can be seen, sensitivity is particularly poor at boric acid concentrations in excess of 20 to 25 μg per ml.

Curve G is that published for the Chromotrope method.[2] Since it lies roughly parallel to F it cannot be claimed to indicate superior sensitivity.

The fragments of wood were ashed at 600° C in porcelain crucibles, after addition of 2 ml of 0·2 per cent. barium hydroxide solution. The residue was triturated with 2 ml of 0·36 *N* sulphuric acid, and 1 ml of the clear solution was used after centrifugation. The entire length of curve F was used, and maximum sensitivity attained where it is most needed, *viz.*, for low concentrations of boron.

The standard curve was checked from time to time and found to be reproducible. The recovery of boron from a range of synthetic samples was at least 93 per cent. and the reproducibility on unknowns was adequate, the average deviation from the mean being about 2 per cent.

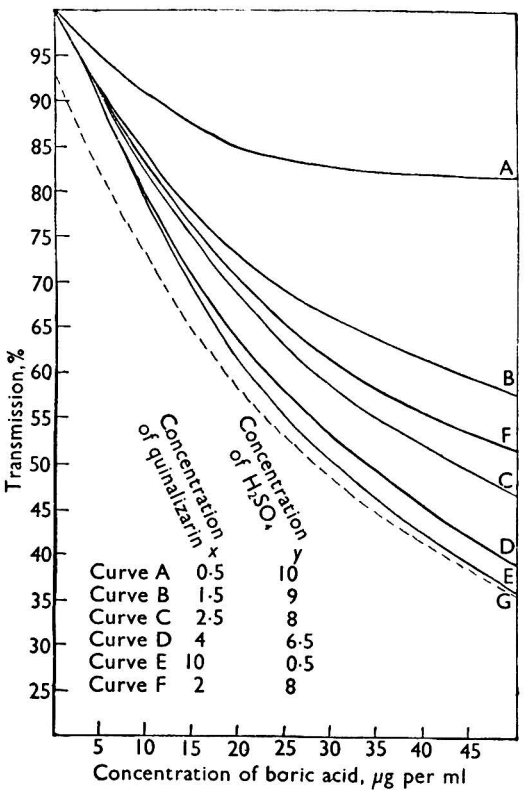

Fig. 1. Effect of quantity of reagent on sensitivity.
Volume of 0·01 per cent. quinalizarin solution = x ml.
Volume of concentrated sulphuric acid = y ml

The author thanks the Director, Dominion Laboratory, New Zealand D.S.I.R., for permission to publish this note, and the Director, Plant Diseases Division, for the loan of a spectrophotometer.

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Appendix

When this note was ready for despatch, the paper by D. MacDougall and D. A. Biggs (*Anal. Chem.*, 1952, **24**, 566) on the estimation of boron in plant tissue by a modified quinalizarin method was received. These authors report similar conclusions, and suggest a reagent containing 45 mg of quinalizarin per litre of 96 per cent. sulphuric acid. As the findings and experiences recorded in the above note are complementary to those of MacDougall and Biggs, and since British analytical

reagent grade sulphuric acid is at least 99 per cent. w/w in strength, the note may yet be of interest, and the colorimetric procedure that it describes may find favour.

The Spekker photo-electric absorptiometer, with an Ilford No. 607 colour filter (575 to 650 mμ) and 1-cm cuvettes, has also been used successfully. The reference standard was first balanced with a drum setting of 0·300. The following calibration readings were obtained—

Boric acid concentration, μg per ml ..	0	10	20	30	40	50
Drum reading	0·300	0·182	0·119	0·071	0·033	0·013

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July 9th, 1952

FEIGL'S MICRO-TEST FOR MERCURY IN ORGANIC SUBSTANCES

FEIGL[1] describes a micro-test for organic mercury in which the substance is mixed and covered with copper oxide and then heated in a micro-crucible carrying a disc of filter-paper treated with palladous chloride; the escaping vapours of mercury leave a dark stain of reduced palladium on the paper. The stain can be intensified by subsequently exposing the paper to ammonia vapour, which forms a colourless compound with the excess of palladous chloride.

The following organic mercury compounds were used to check the test: acetoxymercuryethylacetate,[2] aceto(2-chloromercuryethyl)-mesidide,[3] bromomercuryethylpyridine bromomercuriate,[3] iodomercuryethylpyridine iodomercuriate,[3] bicamphor-10-mercury,[4] camphor-10-mercury iodide[4] and bis-3-chlorocamphor-10-mercury.[5]

Palladous chloride was used many years ago by Merget[6] to show the presence of mercury vapours in the atmosphere of a mirror factory, but his test did not come into general use.

Acetoxymercuryethylacetate, aceto-(2-chloromercuryethyl)-mesidide, bromomercuryethylpyridine bromomercuriate and iodomercuryethylpyridine iodomercuriate, like many organic mercury compounds of similar structure, evolve ethylene easily, even on heating with copper oxide; this is apt to lead occasionally to high nitrogen values in micro-Dumas estimations. As ethylene also reduces palladous chloride[7] the vapours were first intercepted by a gold leaf* placed above the copper oxide mixture. However, no ethylene could be detected from these four substances with palladous chloride. The mercury vapours that are released but slowly during the decomposition of the organic substance can be more rapidly liberated by heating the gold leaf; since they do not affect palladous chloride below a certain threshold concentration,[1] the sensitivity of the test is, although not substantially improved, made more independent of the procedure.

METHOD—

Apparatus—A Pyrex-glass ignition tube held in a hole in a piece of asbestos board so that the open top is protected from the heat of a bunsen burner below.

Procedure—Mix a small amount of the test substance, corresponding at least to 1 μg or, better, to several micrograms of mercury, with a few hundredths of a gram of copper oxide, put the mixture into a Pyrex $1\frac{3}{4} \times \frac{3}{8}$-inch ignition tube and cover it completely with copper oxide. Place the tube in the hole in the asbestos board, which should rest on a tripod. Adjust the tube with the bottom protruding below the board. Add to a circular piece of filter-paper, of a diameter a little exceeding the external diameter of the tube, one or two drops of an approximately 1 per cent. w/v solution of palladous chloride and place the paper horizontally over the mouth of the tube. Heat the tube carefully by gradually increasing a small bunsen flame until the bottom of the tube is red hot. It is advisable to start with the flame well below the tube and to lift it slowly before increasing it. A dark stain sharply outlining the aperture of the tube indicates the presence of mercury. If in doubt, hold the paper over an open bottle of ammonium hydroxide. The yellowish-brown colour of the paper is discharged and the stain becomes more obvious. Great care has to be taken that the top part of the ignition tube does not become hot, or the palladous chloride may be reduced by the material of the paper.

If only traces of mercury are expected or there is a chance of generating ethylene, place a crushed gold leaf in the upper part of the ignition tube, which can conveniently have a constriction about one-third from its bottom to support the leaf. Decompose the substance as before without warming the gold leaf, which should therefore be sufficiently far above the asbestos board. After decomposing the substance (this takes about 2 minutes) push the tube further down so that the

* Michael Faraday was apparently the first to collect mercury vapours on a gold leaf (see Faraday's Diary, I, Bell and Sons, London, 1932, pp. 132 and 133).

gold leaf can be heated with the full flame for a short time. The palladous chloride paper should be applied only in connection with the second heating.

RANGE—

In experiments with a gold leaf, 1 μg of mercury could be detected even when the amount of the organic component was increased, *e.g.*, by adding phthalic anhydride to acetoxymercuryethylacetate. But sometimes even smaller quantities produced a distinct mark on the paper. Only with iodomercuryethylpyridine iodomercuriate, which contains four atoms of iodine for two mercury atoms, was the lower limit 4 μg, apparently because some mercury was liberated in the form of mercuric iodide. This limitation could be obviated by using *cuprum praecipitatum* instead of copper oxide to cover the mixture in the ignition tube, when the limit is brought down to 2 μg.

The author acknowledges with gratitude his indebtedness to Dr. J. D. Loudon for the gift of specimens of bicamphor-10-mercury, camphor-10-mercury iodide and bis-3-chlorocamphor-10-mercury.

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4. Loudon, J. D., *Ibid.*, 1933, 825.
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CHEMISTRY DEPARTMENT
THE UNIVERSITY OF GLASGOW

G. SACHS
September 10th, 1952

ANHYDROUS CALCIUM OXALATE AS A WEIGHING FORM FOR CALCIUM

DUVAL[1] has shown that the thermolysis curve obtained by heating hydrated calcium oxalate exhibits a horizontal section, between 226° and 398° C, corresponding to anhydrous calcium oxalate. He makes the comment: "This provides a second method for determining calcium, a method which is too seldom used."

We have recently found an average error of +0·7 per cent. in determining 90 mg of calcium by this method, the reason being that anhydrous calcium oxalate, on exposure to the atmosphere, absorbs water fairly rapidly until the monohydrate is re-formed. Care is therefore required in using the anhydrous salt as a weighing form.

REFERENCE

1. Duval, C., *Anal. Chem.*, 1951, **23**, 1271.

CHEMISTRY DEPARTMENT
THE UNIVERSITY
EDINBURGH

C. C. MILLER
August 21st, 1952

Ministry of Food

STATUTORY INSTRUMENTS*

1952—No. 2257. The Meat Products (No. 3) Order, 1952. Price 4d.

This Order, which came into operation on January 1st, 1953, replaces the Meat Products (No. 2) Order, 1952 (S.I., 1952, No. 1124; Analyst, 1952, 77, 442), as amended. Under this Order the minimum meat content requirements for uncooked pork sausages, beef sausages and sausage meat are retained, but the minimum meat content requirements prescribed in the No. 2 Order for other meat products are not renewed.

1953—No. 210. The Oils and Fats Order, 1953. Price 4d.

This Order, which came into operation on February 15th, 1953, replaces the Oils and Fats Order, 1952 (S.I., 1952, No. 327), as amended (S.I., 1952, No. 1773). Under defined conditions certain fats previously reserved for industrial use are now permitted to be used for food.

1953—No. 245. The Canned Corned Meat (Prices) Order, 1953. Price 3d.

This Order, which came into operation on March 1st, 1953, revokes the Meat Products (No. 3) Order, 1952 (S.I., 1952, No. 2257; see above). Price and other controls are removed from uncooked sausages and sausage meat but retail price control is retained over canned corned meat.

1953—No. 246. The Offals in Meat Products Order, 1953. Price 3d.

This Order, which came into operation on March 1st, 1953, states that no person shall use or cause or permit to be used any prohibited offal in the composition or preparation of any uncooked open meat product intended for sale or sold for human consumption.

"Open meat product" means any food used, manufactured or prepared for human consumption which is manufactured or prepared from meat and another ingredient or other ingredients and which is not and has not been canned.

"Prohibited offals" means brains, feet, fries, gut (including chitterlings), manifolds, paunches, udders, sweetbreads, tripe, melts or lites, spinal cord, uteri, pigs' maws and calves' vells.

FOOD STANDARDS COMMITTEE

TIN IN CANNED FOODS

THE Minister of Food has approved for publication a Report presented to the Food Standards Committee by its Metallic Contamination Sub-Committee in respect of the limits of tin in canned foods.

The Sub-Committee point out that the limit of 2 grains per lb (286 p.p.m.), which was recommended in 1908 in a Report published by the Local Government Board, has been generally regarded as satisfactory and that there is hardly any evidence of poisoning attributable to excessive tin content in canned foods. They suggest that a limit should be maintained, as a high tin content in food would be contrary to good commercial practice and possibly injurious. In view of improvements in the canning process since 1908, the Sub-Committee recommend that the figure should be reduced to 250 p.p.m. Until more decisive information is available on the subject of toxicity, the Sub-Committee do not consider it necessary to give statutory effect to the proposed limit of 250 p.p.m.

British Standards Institution

AMENDMENT SLIP†

A printed slip bearing Amendments to a British Standard has been issued by the Institution, as follows—

PD 1551—Amendment No. 1 (December, 1952) to B.S. 1900 : 1952. Secondary reference thermometers (Centigrade scale).

DRAFT SPECIFICATION

A FEW copies of the following draft specification, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, Society of Public Analysts and Other Analytical Chemists, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee OSC/4—Essential Oils.
CO(OSC)9397—Draft B.S. for Methods of Testing Essential Oils.

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

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

Book Reviews

BIOCHEMICAL PREPARATIONS. Volume II. Edited by E. G. BALL. Pp. viii + 109. New York: John Wiley & Sons Inc. London: Chapman & Hall, Ltd. 1952. Price 24s.; $3.00.

The first volume of "Biochemical Preparations" was published in 1949, and it was the intention of its Editorial Board to produce additional volumes at intervals of 12 to 18 months. However, 3 years have elapsed between the publication of Volumes I and II, an indication, no doubt, of the difficulties encountered in producing books of this type.

The format and arrangement of this book follow precisely those of Volume I and are similar to those adopted for the older "Organic Syntheses" and "Inorganic Syntheses."

The subjects of the monographs in this volume are as varied as were those of Volume I (see *Analyst*, 1950, **75**, 57), although there is a general resemblance between the subject-matters of the two volumes. Thus, in both volumes several of the preparations are of phosphates of biological interest, Volume II dealing with the preparation of phosphoryl-enolpyruvic acid, L-α-glycerophosphoric acid, glucose-6-phosphate, fructose-1:6-diphosphate, inositol monophosphate and phosphorylcholine. Again, both volumes describe the preparation of a limited number of amino-acids, peptides and proteins. In the present volume, the syntheses of DL-glutamic acid monohydrate, L-aspartic acid and glutathione and its intermediates are described, together with the extraction of cytochrome *c* from minced muscle, globulin from cucurbit seed and phosvitin from egg yolk.

One of the most interesting and unusual monographs describes the preparation of ^{14}C uniformly-labelled sucrose; a carbohydrate-depleted *Canna* leaf is placed in a photosynthesis chamber filled with $^{14}CO_2$ and the sucrose formed is extracted and purified. It is surprising to learn that one *Canna* leaf weighing only 6 g yields as much as 405 mg of radioactive sucrose by this method.

The book is well up to the high standard of the first volume and that of the series of "Organic Syntheses," now so indispensable to the organic chemist. It is well printed and the binding excellent, although the price of the present volume seems rather high in relation to that of Volume I, even when allowance is made for the increase in size. Nevertheless, if the standards established for the first two volumes of the series are maintained in succeeding volumes, there is little doubt that "Biochemical Preparations" will become as indispensable to the biochemist as the related series has become to the organic chemist, and it is to be hoped that the delay in publishing Volume III will be considerably less than that involved in issuing the present volume.

F. A. ROBINSON

Publications Received

PROGRÈS RÉCENTS DE LA CHROMATOGRAPHIE. Deuxième Partie. CHIMIE MINÉRALE. By MICHAEL LEDERER. Pp. 131. Paris: Hermann et Cie. 1952.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. Pp. 179. London: Association of British Chemical Manufacturers. 1953. Gratis.

VISUAL LINES FOR SPECTROSCOPIC ANALYSIS. By D. M. SMITH, A.R.C.S., B.Sc., D.I.C., F.Inst.P. Second Edition. Pp. 102. London: Hilger & Watts Ltd. 1952. Price 16s.

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS. By I. M. KOLTHOFF, Ph.D., and E. B. SANDELL, Ph.D. Third Edition. Pp. xvi + 759. New York and London: Messrs. Macmillan & Co. Ltd. 1952. Price 30s.

FERTILISERS. METHODS OF ANALYSIS USED IN O.E.E.C. COUNTRIES. Pp. 182. Paris: The Organisation for European Economic Co-operation. 1952.

GENERAL AND INORGANIC CHEMISTRY. By ALEXANDER FINDLAY, C.B.E., M.A., D.Sc., LL.D. Pp. xvi + 239. London: Methuen & Co. Ltd. 1953. Price 8s. 6d.

INORGANIC THERMOGRAVIMETRIC ANALYSIS. By CLÉMENT DUVAL. Pp. xvi + 531. Amsterdam, London and New York: Elsevier Publishing Co. Ltd. London: Cleaver-Hume Press Ltd. 1953. Price 60s.

ORGANIC SYNTHESES. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 32. Editor-in-Chief: R. T. ARNOLD. Pp. vi + 119. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1952. Price 28s.; $3.50.

ASSISTANT CHEMIST required for a fuel and engine testing laboratory at Bletchley. Previous experience in inorganic analyses is necessary and a University degree or A.R.I.C. qualification is preferred, but not essential. Starting salary £550–£650 per annum according to age, qualifications and experience. The selected applicant will be eligible to join the Company's contributory pension scheme. Applications giving brief particulars of age, education, qualifications and experience should be sent to Box No. 320, E.C. Advertising Co., 54, Old Broad Street, London, E.C.2.

THE Directors of the Co-operative Wholesale Society Ltd. invite applications for the position of Chief Chemist for their Preserves Group of Factories. Candidates must have experience in the trade, and the apointee would be expected to collaborate with Management on raw material purchases and control, supervise routine laboratory work, and be capable of initiating and developing new lines in the various production departments involving Jams, Pickles, Sauces and Canning.

Applications, stating age, education, experience, qualifications, and salary required, should be addressed to the C.W.S. Ltd., Central Labour Department, 1, Balloon Street, Manchester, 1, endorsed "Chief Chemist—Preserve Factories."

A METALLURGICAL Chemist is required by Allied Ironfounders Ltd. to take charge of the Chemical Laboratory for the Shropshire Group of Companies.

The applicant, preferably between 30 and 40 years of age, will require as minimum qualifications National Certificate, experience in cupola control, an appreciation of the influence of elements on grey and high duty irons, along with the ability to make up cupola charges, and to control small staff in the analysis of cast metal.

Salary will depend on qualifications and help will be given with housing.

Apply with full details of qualifications to Allied Ironfounders Ltd. (R.W.S. Dept.), Ketley, Wellington, Shropshire.

ASSISTANT to specialise in clinical biochemical analysis required in London. Salary according to age and experience but not less than £400 p.a. Write Box No. 3838, THE ANALYST, 47, Gresham Street, London, E.C.2.

ASSISTANT for Analytical Laboratory in S.E. London. Of Inter B.Sc. or Higher Nat. Cert. (Chem.) Standard. Must have completed Military Service. Pension Fund. Write Box 3836, THE ANALYST, 47, Gresham Street, London, E.C.2.

HOPKIN & WILLIAMS LTD., Uphall Road, Ilford, Essex, have a vacancy for a young qualified chemist in the Works Control Test Laboratory. Applications should be by letter giving particulars of qualifications and experience and addressed to the Works Manager.

ANALYST. May & Baker, Ltd., Dagenham, Essex, have a vacancy in their Analytical Development Laboratory for an assistant holding either the B.Sc., A.R.I.C.I., B.Pharm. or Ph.C. qualification for non-routine analysis and analytical research. Salary according to age, qualifications and experience. Contributory Pension Scheme. Five day week. Apply initially in writing to the Personnel Officer, quoting reference No. 35.

SOUTHERN RHODESIA GOVERNMENT
VACANCY : CHIEF CHEMIST : GEOLOGICAL SURVEY

APPLICANTS, under 43, should possess an honours degree in chemistry with experience in inorganic analysis. Knowledge of spectrographic analysis would be a strong recommendation.

Salary Scale: £1,530 x £48 to £1,722 x £72 to £1,938 p.a.

Application forms and further details from the Secretary, Rhodesia House, 429, Strand, London, W.C.2. Completed forms to be returned by April 10.

ANALYTICAL CHEMIST, B.Sc. or A.R.I.C., required for large food factory in the Midlands. Experience preferred but not essential. Salary according to qualifications and experience. Write Box No. 3839, THE ANALYST, 47, Gresham Street, London, E.C.2.

HER MAJESTY'S COLONIAL SERVICE

A VACANCY exists for a Chemist/Assayer (27106/57/52) in Northern Rhodesia. The appointment is on agreement for one tour of three years in the first instance with salary in the scale £690–£1,320 according to qualifications and experience. In addition a cost of living allowance of 21 per cent. of salary is payable. Income tax at low local rates; Water, light and sanitary fees also payable; Rent for Government quarters with heavy furniture, when available, not more than 10 per cent. of salary; Free passages for officer, wife and up to the cost of one adult return passage for children; Free medical attention for officer and family within Northern Rhodesia; Five days vacation leave for each completed month of resident service. Candidates, preferably between 25 and 30 years of age, should possess an Honours degree in Chemistry and would be required to undergo two years' special post-graduate training before taking up appointment. Duties will be to carry out assays and analyses of ores, minerals and rocks in the laboratory of the Geological Survey Department. Apply in writing to the Director of Recruitment, Colonial Office, Great Smith Street, London, S.W.1, giving briefly age, qualifications and experience. Mention the reference number (27106/57/52).

FOR SALE. Analyst 1943–1950, indexed, bound. 1951 loose. Perfect condition. Best offer. Box No. 3837, THE ANALYST, 47, Gresham Street, London, E.C.2.

BOOKS URGENTLY WANTED SCHOELLER & POWELL, The Analysis of Minerals and Ores of the Rarer Earths. 1940. Also SCHOELLER, Analytical Chemistry Tantalum and Niobium (Chapman Hall, 1937). Offers to Malcolm Gardner, 12, Earnshaw Street, London, W.C.2.

THE proprietors of British Patent No. 648887 are prepared to sell the patent or to licence British Manufacturers to work thereunder. It relates to a FLOAT BALANCE FOR MEASURING WEIGHTS OR FORCES.

Address: Boult, Wade & Tennant, 112, Hatton Garden, London, E.C.1.

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