THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held on Wednesday, November 5th, 1947, at 6 p.m., in the Chemical Society's Rooms, Burlington House, London, W.1. The President, Mr. Lewis Eynon, was in the Chair. The following papers were read and discussed :—" The Determination of Arsenic Pentoxide in White Arsenic," by D. A. Lambie; " A Semi-micro Combustion Method for the Determination of Organic Carbon," by J. B. Rickson; " Some Observations on the Semi-micro Determination of Carbon and Hydrogen by the Sucharda and Bobranski Method, using a Macro-Balance," by Frank Goulden.

NEW MEMBERS

Frank John Allen, A.R.I.C.; Donald Wheeler Browne, B.Sc., Ph.D. (Lond.); Edwin Dawson Chilwell, B.Sc. (Lond.), A.R.I.C.; Gerald Harry Edwards, B.Sc. (Lond.), F.R.I.C.; Kenneth Sydney Fowler, B.Sc. (Reading), A.R.I.C.; Philip Harry Freestone, B.Sc. (Lond.), A.R.I.C.; Peter Fuller; Ralph Goulden, A.R.I.C.; Walter Hirsch, D.Phil.nat. (Frankfurt); Mervyn Henry Jenkins, B.Sc. (Pretoria); Mrs. Bertha Lamb, B.Sc. (Lond.); James Muil Leitch, B.Sc. (Glas.), A.R.I.C.; Douglas Breed Rogers; Leonard Seal, A.Met. (Sheff.); Mohamed El Shahat, M.Pharm., D.Biochem.; Herbert Timmington, B.Pharm., Ph.C.; John George Waller, B.Sc. (Lond.), A.R.I.C., A.R.C.S.

NORTH OF ENGLAND SECTIONS

A MEETING of the Section was held at Manchester on Saturday, April 19th, 1947. The Chairman, Mr. C. H. Manley, presided over an attendance of thirty-six. The following papers were presented and discussed :—" The Determination of Organic Phosphorus," by C. H. Manley, M.A., F.R.I.C. and H. Lobley; " Ice Cream," by E. L. E. Humphries, A.R.I.C.

MICROCHEMISTRY AND PHYSICAL METHODS GROUPS

A JOINT meeting of the Physical Methods Group with the Microchemistry Group was held on Friday, September 26th, 1947, in the Chemical Lecture Theatre of the University Chemical Laboratories, Cambridge. The chair was occupied by Mr. R. C. Chirnside and the attendance numbered eighty. The following papers were presented and discussed :—" Micro-methods of Molecular Weight Determination," by Cecil L. Wilson, M.Sc., Ph.D., F.R.I.C.; " Turbidimetric Methods used in Agricultural Analyses," by J. Tinsley, B.Sc., Ph.D., F.R.I.C.; " Microchemical Applications of Potentiometry," by J. T. Stock, M.Sc., F.R.I.C.; " Micro-Analyses using X-ray Diffraction Technique," by H. P. Rooksby, B.Sc., F.Inst.P.

The meeting was preceded by visits to the Colloid Science Department and the Radio-Chemistry Laboratory of the University.

POLAROGRAPHIC DISCUSSION PANEL of the PHYSICAL METHODS GROUP—Meetings of the Panel were held on July 25th, at University College, London, and on October 3rd, at Norwood Technical College. The discussion at the former meeting was opened by Professor J. Heyrovský and Dr. R. Brdička, and that at the latter by Mr. A. S. Nickelson, Mr. L. Airey and Dr. F. J. Bryant.

The Direct Colorimetric Determination of Tungsten in Cast Iron

By W. WESTWOOD and A. MAYER

A NUMBER of gravimetric procedures have been used by various authors; these include precipitation of tungstic oxide by means of nitric acid, cinchonine,[1] rhodamine B,[2] tannin-phenazone,[3] tannin-antipyrene,[4] benzidine[4] and 8-hydroxyquinoline.[4,5] All these methods have the disadvantage that with small amounts of tungsten precipitation is incomplete; also the final product is usually contaminated by small amounts of various elements such as iron, molybdenum, chromium, vanadium, silicon, titanium and zirconium, which necessitate its purification. Moreover, the conversion factor of tungstic oxide to tungsten, 0·7931, is very high. A volumetric method has been described,[6] in which reduction by means of lead amalgam is followed by titration with permanganate; but this method also requires complete preliminary separation of tungsten.

Several colorimetric methods are available in which reduction of tungstic oxide with stannous chloride[7] or titanium trichloride[8] yields blue colloidal lower oxides, but the sensitivity of these reactions is not very great. Dithiol[9] gives with tungstate a blue colloidal precipitate, but molybdenum interferes by forming a green precipitate. A method depending on formation of the dithiol - tungsten complex at elevated temperature and its extraction with amyl acetate has been described recently[10]; molybdenum must first be removed by a similar procedure carried out at room temperature. A rough colorimetric method makes use of the violet colour given by a tungstate with rhodamine B in dilute hydrochloric acid.[11] Hydroquinone[12,13,14] in concentrated sulphuric acid has been used extensively as a colorimetric reagent for tungsten. This reaction is interfered with by titanium, which also yields a brown colour. The two colours can be differentiated by measurement of the absorption at different wavelengths, but the method is tedious and requires separation of the tungsten from iron. Niobium, moreover, behaves much like tungsten in this reaction.

The yellow or green colour formed by thiocyanate with tungsten in presence of a reducing agent has been the subject of much study,[15,16,17,18,19,20,21] and various conditions have been prescribed for the reaction. We have previously used this reaction as the basis of a method for determining tungsten in cast iron.[18] The necessity for preliminary separation from iron and other elements, which led to low results when the tungsten present was less than 0·5 per cent., besides other minor disadvantages, rendered it not wholly satisfactory. An attempt to improve the method by extracting the colour (produced by adding sodium thiocyanate, stannous chloride and hydrochloric acid to a standard tungstate solution and then heating on a water-bath) by means of organic solvents such as ether, *cyclo*hexanol, butyl acetate or, better, amyl acetate, was partially effective. Variations in the intensity and rate of the colour development consequent on small changes in the concentration of reagents and the period of heating made it difficult to obtain reproducible results. In the course of these experiments it was noticed that heating was not necessary when the hydrochloric acid content was more than 70 per cent. of the concentrated acid by volume and that the yellow colour was more stable when it was formed in the cold. For example, a solution containing 0·4 mg. of tungsten as sodium tungstate, prepared by dissolving 0·1261 g. of pure dry tungstic oxide, WO_3, in a little sodium hydroxide and diluting to a litre (1 ml. ≡ 0·1 mg. of tungsten) was placed in a beaker; to this were added 6 ml. of water, 1·5 ml. of sodium thiocyanate solution (500 g. per litre), 5 ml. of stannous chloride solution (200 g. in 1 litre of hydrochloric acid), and 15 ml. of hydrochloric acid. A yellow colour developed on standing. It was measured at intervals on a Spekker absorptiometer, using a 2 cm. cell and Ilford violet filters No. 601. The colour reached its maximum intensity in 17 minutes and remained stable for at least an hour. This result was sufficiently satisfactory to warrant a full investigation to establish the optimum conditions.

Experimental

Influence of thiocyanate concentration on the intensity of the colour—Different amounts of sodium thiocyanate solution (500 g. per litre) ranging from 0·5 to 3·5 ml. were added to a standard tungsten solution together with the reagents used in the preliminary experiment above. With each experiment a "blank" without tungsten was carried out. The results

(see Table I) show that the "blanks" developed a colour (brown) when more than 2 ml. of thiocyanate solution were present, and that the optimum amount of thiocyanate solution was 1·0 to 1·5 ml., *i.e.*, 0·75 g. to 1·25 g. of sodium thiocyanate, in 50 ml. of solution.

TABLE I

INFLUENCE OF THIOCYANATE CONCENTRATION

NaCNS solution ml.	Standard tungsten solution ml.	Drum reading
0·5	2·0	0·73
0·5	nil	1·00
1·0	2·0	0·545
1·0	nil	0·995
1·5	2·0	0·535
1·5	nil	0·995
2·0	2·0	0·515
2·0	nil	0·97
2·5	2·0	0·50
2·5	nil	0·95
3·5	2·0	0·435
3·5	nil	0·89

Influence of hydrochloric acid concentration on the colour—It was known from previous observations that variation of the hydrochloric acid concentration had pronounced effects on the intensity of the colour. This effect was investigated in detail as follows. To a series of solutions of similar tungsten content were added 1·5 ml. of the thiocyanate solution, and 20 ml. of hydrochloric acid of varying concentration, followed by 5 ml. of the stannous chloride solution. The total volume was kept constant throughout. After standing for 17 minutes the colours were measured on the Spekker absorptiometer in the usual manner. The results, given in Table II, show that the optimum concentration of hydrochloric acid lies between 70 and 80 per cent. of the concentrated acid in the final reaction mixture.

TABLE II

INFLUENCE OF HYDROCHLORIC ACID CONCENTRATION

Hydrochloric acid, per cent. v/v of conc. acid	Appearance of solution	Drum reading
16	Colourless	0·99
30	Colourless	0·98
40	Very slightly yellow	0·97
50	Yellow	0·88
60	Yellow	0·86
70	Yellow	0·60
80	Yellow	0·59
90	Precipitate (probably NaCl)	0·615 (after filtration)

In subsequent experiments the reaction solutions were always diluted to a standard volume, 50 ml.

Influence of concentration of stannous chloride reagent on the colour—This was investigated by taking 3 ml. of the standard tungsten solution, diluting to 10 ml. with water, adding 1·5 ml. of the thiocyanate solution and varying amounts (2 to 12 ml.) of stannous chloride reagent (250 g. in 1 litre of hydrochloric acid) and diluting to 50 ml. with hydrochloric acid. This gave an acidity of 77·5 per cent. in terms of concentrated hydrochloric acid. The intensity of the colour increased with increasing amounts of stannous chloride solution up to 9 ml. Further additions up to 12 ml. had no further effect.

For subsequent experiments the stannous chloride and hydrochloric acid were combined in a single reagent. The new stannous chloride reagent contained 70 g. of stannous chloride in 1 litre of hydrochloric acid.

Development of the colour with time—This was investigated by observing the drum reading at regular intervals for two solutions of tungsten, one containing 0·1 mg. and the other 0·6 mg. The curves obtained are shown in Fig. 1. Development of the colour, both for large and small amounts of tungsten, is complete within 17 minutes and then remains constant for at least 2 hours.

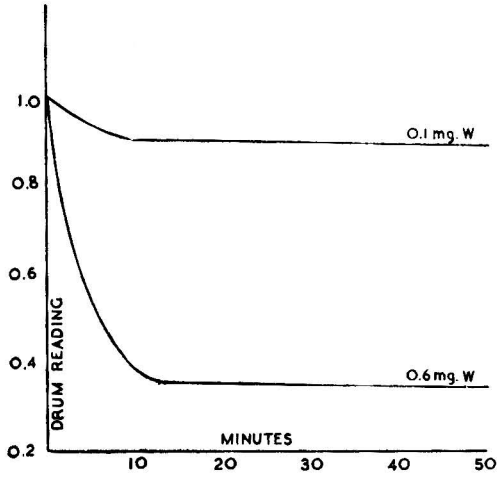

Fig. 1. Development of colour with time.

CALIBRATION GRAPH—A preliminary calibration graph was constructed based on various amounts of standard tungsten solution made up to 10 ml. with water, to which were added 1·5 ml. of sodium thiocyanate solution (500 g. per litre) and sufficient stannous chloride reagent (70 g. in 1 litre of concentrated hydrochloric acid) to make 50 ml. in a graduated flask. The colour was allowed to develop for 20 minutes and the absorption measured on the Spekker absorptiometer, using 2 cm. cells and violet filters No. 601. The graph was a straight line and entirely reproducible. It conformed to the equation

$$\text{Tungsten per cent.} = (0{\cdot}96 - \text{drum reading})/1{\cdot}103$$

The colours were stable for at least 2 hours. The range of tungsten that could be determined under these conditions was 0 to 0·87 mg.

From the investigation described above it appeared possible that the method could be adapted readily to the direct determination of tungsten in cast iron. For this purpose the effects of various alloying elements and other ions were investigated. To prevent precipitation of tungstic oxide during dissolution of the sample in acid, it was advisable to have tartaric acid present, which would form a complex with tungstate. The tartrate, when tried on pure solutions, did not interfere with the colour development.

EFFECT OF ALLOYING ELEMENTS AND OTHER IONS—

Iron—Iron is without effect. A calibration graph was prepared under the same conditions as before (above), except that the solutions contained, also, 0·1 g. of iron as ferric chloride and 1 g. of tartaric acid, added before developing the colour. The iron underwent reduction immediately and the graph was found to be identical with that for a pure tungsten solution.

Molybdenum—Solutions of molybdate were added to a synthetic sample solution containing 0·1 g. of iron, 1 g. of tartaric acid, and the usual reagents. On addition of the stannous chloride, the deep red ferric thiocyanate colour disappeared immediately, whereas the amber-coloured molybdenum thiocyanate persisted for about a minute and then faded rapidly. At the end of 20 minutes the colours had faded almost completely to a faint yellow. The drum difference readings for quantities of molybdenum corresponding to 0·5, 1·0, 2·0, 2·5, and 3·0 per cent. on a 0·1-g. sample of iron were 0·005, 0·01, 0·02, 0·025, and 0·03 respectively. These readings showed that amounts of molybdenum normally present in cast iron did not interfere; larger amounts could be allowed for by using a correction graph (1 per cent. of Mo $\equiv$ 0·009 per cent. of W). The persistence of the amber colour of the molybdenum complex for a few minutes serves to indicate the presence of molybdenum.

Other cations—The possible interference of a number of elements was investigated by adding them to tungsten-free solutions containing 0·1 g. of iron and treating with the usual reagents (see Table III). No interference was encountered from aluminium, antimony, bismuth, lead, manganese, titanium or zirconium in the maximum amounts normally present in cast iron. Chromium, large amounts of cobalt, nickel and vanadium interfered by the formation of coloured ions. Arsenic, selenium and tellurium were reduced to the elements, giving brown colours or precipitates. Copper formed a precipitate of cuprous thiocyanate.

Chromium, cobalt, nickel, tellurium and vanadium can be corrected for by a difference method. This involves measurement of the colour of the final solution containing all reagents except the thiocyanate as described in the procedure (p. 468).

It was found that arsenic below 0·05 per cent. and copper below 0·5 per cent. did not interfere.

Selenium, if present, and copper and arsenic in excess of the amounts mentioned must be removed.

Anions—Phosphate (≡ 2 per cent. of P) and sulphate did not interfere. In presence of fluoride or nitrate, colour development was almost completely inhibited.

TABLE III

EFFECTS OF VARIOUS ELEMENTS

Element	Quantity taken, as per cent. on a 0·1-g. sample of iron	Observation	Drum reading
Manganese	2·2	Colourless	1·00
Aluminium	6·0	Colourless	1·00
Titanium	1·0	Colourless	1·00
Vanadium	1·0	Yellow	0·79
Nickel	10·0	Very slight green	0·955
Lead	0·5	Colourless	1·00
Zirconium	1·5	Colourless	1·00
Bismuth	0·5	Colourless	1·00
Arsenic	0·4	Brown precipitate	0·44
Antimony	1·5	Colourless	1·00
Cobalt	3·0	Very slight green	0·975
Copper	4·0	White precipitate	Too dense to read
Chromium	4·0	Greenish	0·90
Selenium	0·2	Orange turbidity	0·86
Tellurium	0·2	Brown colour	0·92

DEVELOPMENT OF COLOUR WITH TIME—This had been investigated previously, with pure solutions, but it was necessary to find out whether the rate of colour development was affected by the presence of tartrate and iron. The results obtained with a solution containing 0·1 g. of iron, 1 g. of tartaric acid, 0·8 mg. of tungsten as sodium tungstate and the usual reagents, are shown in Table IV.

TABLE IV

RATE OF DEVELOPMENT OF THE COLOUR

Time in minutes	Drum reading	Apparent tungsten present, mg.
0	1·00	0·00
2	0·46	0·46
2·5	0·42	0·49
3·5	0·355	0·55
4·5	0·315	0·585
5·5	0·275	0·62
6·5	0·24	0·655
7·5	0·218	0·675
8·5	0·20	0·690
9·5	0·17	0·715
11·5	0·15	0·735
12·5	0·135	0·745
16·5	0·09	0·785
20·0	0·075	0·80
30·0	0·075	0·80

The presence of other ions had very little effect on the rate of development of the colour with time. Twenty minutes is the time necessary for complete colour development.

TEMPERATURE—The effect of the temperature of the solution at the time of colour development was investigated by adding the usual reagents to a standard tungsten solution and heating the hydrochloric acid before addition. It was found that the rate of development of the stable colour was not affected by variations of temperature between 15° and 40° C.

It appeared, however, that the intensity of the final colour varied slightly with the temperature of the stannous chloride - hydrochloric acid reagent. It was advisable to adjust the temperature of the reagent to within ±2° C. of a convenient temperature, say 20° C.

APPLICATION TO CAST IRON—

The method was next applied to samples of tungsten-free iron to which increasing amounts of standard tungsten solution were added. One g. of sample plus tungsten solution

was dissolved in hydrochloric acid in presence of tartaric acid, filtered through a pad and diluted to 100 ml. A 10-ml. portion, equivalent to 0·1 g. of sample, was placed in a 50-ml. graduated flask. To this was added thiocyanate solution and stannous chloride reagent, and after standing for 20 minutes the colours were measured on the Spekker absorptiometer in the usual manner. Another 10-ml. fraction was treated similarly but the thiocyanate was replaced by 1·5 ml. of water. The difference between the two readings was plotted against the percentage of added tungsten. The graph was identical with that obtained previously. A number of samples of cast iron containing tungsten as an alloying element were then treated by the above procedure. The residues obtained after the first filtration were ignited, treated with hydrofluoric acid to remove silica, fused with sodium carbonate and extracted in hydrochloric - tartaric acid mixture. After making up to 100 ml. a 10-ml. fraction was taken and the tungsten colour developed in the manner described previously. The samples thus treated contained some tungsten in the acid-insoluble portion. The major part of the tungsten appeared to dissolve readily under the given conditions, and it is thought likely that only the tungsten present as carbide did not dissolve. The method, therefore, had to be modified, so as to include the insoluble portion of the tungsten. This was done as indicated above, but the extract was added to the main filtrate before making up to 100 ml.

The proposed method for the determination of tungsten in cast iron is as follows.

METHOD

REAGENTS—*Diluted hydrochloric acid* (1 + 4). *Tartaric acid solution,* 500 g. per litre. *Tartaric acid solution,* 20 g. per litre. *Hydrogen peroxide,* 20 vol. *Sodium thiocyanate solution,* 500 g. per litre. *Stannous chloride solution,* 70 g. dissolved in 1 litre of hydrochloric acid. *Sodium carbonate,* anhydrous. *Hydrofluoric acid. Nitric acid.*

PROCEDURE—Dissolve 1 g. of sample in 30 ml. of diluted hydrochloric acid (1 + 4) and 20 ml. of tartaric acid solution (containing 500 g. per litre). When dissolution is complete add 15 ml. of hydrogen peroxide, boil for 5 minutes, filter through a pad, collecting the filtrate in a beaker, and wash the pad with hot tartaric acid solution containing 20 g. per litre. Reserve the filtrate. Transfer the entire residue to a platinum crucible and ignite at a temperature of less than 750° C. Treat the ignited residue with 2 drops of nitric acid and 5 to 10 drops of hydrofluoric acid and heat to remove silica. Again ignite at less than 750° C. for a few minutes and then fuse the residue with about 1 g. of sodium carbonate. Cool the melt and extract it in the reserved filtrate. Cool and dilute this to 100 ml. in a graduated flask. Pipette a 10-ml. fraction into a 50-ml. graduated flask and add to it 1·5 ml. of sodium thiocyanate solution from a burette. Dilute the solution to 50 ml. with stannous chloride reagent adjusted to 20° C. ±2° C. Prepare a blank solution by taking another 10-ml. fraction, adding to it 1·5 ml. of water and stannous chloride reagent to make up 50 ml. Allow both solutions to stand for 20 minutes and then measure the colours on the Spekker absorptiometer, using 2-cm. cells, Ilford violet filters No. 601, and setting water/water 1·00. The difference of the two readings is a measure of the tungsten content of the sample.

STANDARDISATION—STANDARD TUNGSTATE SOLUTION—Dissolve 1·2610 g. of pure, dry tungstic oxide, WO_3, in 10 ml. of sodium hydroxide solution (containing 10 g. per litre) and dilute to 1 litre. One ml. of this solution is equivalent to 1 mg. of tungsten, *i.e.*, to 0·1-per cent. on a 1-g. sample. Add increasing volumes of this solution to 1-g. samples of tungsten-free cast iron and carry out the normal procedure. Plot the difference drum readings against percentage of tungsten added, to obtain the calibration graph.

In the authors' laboratory this conformed to the equation

$$\text{Tungsten per cent.} = 0{\cdot}906 \times \text{drum reading difference.}$$

NOTES—(1) The method is applicable to all cast iron samples except those containing copper in excess of 0·50 per cent., arsenic in excess of 0·05 per cent. or selenium.

(2) The procedure described gives a graph that covers a range of tungsten from 0 to 0·85 per cent. For amounts in excess of that, a smaller fraction than 10 ml. must be taken and made up to 10 ml. with water; alternatively, a smaller weight of sample may be used.

(3) The stannous chloride reagent should be prepared fresh daily.

(4) Sodium thiocyanate cannot be replaced by potassium thiocyanate because the latter would result in the formation of insoluble potassium tartrate.

(5) Samples that will not dissolve under the conditions described may be treated as follows. Dissolve 1 g. of sample in 30 ml. of diluted hydrochloric acid (1 + 1) and when

dissolution is complete oxidise by addition of nitric acid. Evaporate to dryness, and bake to dehydrate silica and remove nitric acid. Cool, add 10 ml. of hydrochloric acid and digest to dissolve salts. Add 20 ml. of tartaric acid containing 500 g. per litre, heat to boiling and filter. Continue as described in the procedure. In this case most of the tungsten will be in the residue.

The method occupies 1½ hours and is accurate to ±0·01 per cent.

SUMMARY—A method is proposed for determining small amounts of tungsten in cast iron. It depends upon the formation of an intensely yellow-coloured tungsten thiocyanate complex in strong hydrochloric acid solution in presence of stannous chloride. The colour is measured on the Spekker absorptiometer. Alloying elements in amounts normally present in cast iron do not interfere. The method is speedy and has been found to yield accurate and reproducible results.

The authors wish to express their thanks to the Director and Council of the British Cast Iron Research Association for permission to publish this work.

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THE BRITISH CAST IRON RESEARCH ASSOCIATION
ALVECHURCH, BIRMINGHAM

January, 1947

The Determination of Mercury by means of Dithizone

BY H. BARNES

THE following notes, based on the experience of several years' use of dithizone for routine and other determinations, are prompted by the paper of Milton and Hoskins[12] on the estimation of mercury by a modification of the method of Reith and van Dijk.[13] It is not intended in any way to criticise their paper, but rather to amplify certain of the points raised with a view to assisting other users of this reagent. Further details of the technique used and an account of the separation of mercury from copper by a simple dithizone method involving the use of potassium cobalticyanide, have already been given by Barnes.[1,2]

The routine work has been largely concerned with the determination of the rate of release of mercury from anti-fouling compositions into sea water, and in these routine determinations 100 ml. of solution containing from 1 to 5 μg. of mercury are extracted with 10 ml. of a chloroform solution of dithizone of approximate strength 20 mg. per litre.[6] Dithizone has also been used for determining mercury in small paint samples when 100 ml. of solution, adjusted to contain approximately 100 μg. of mercury, are extracted with 50 ml. of a chloroform solution of dithizone of the above strength. Subsidiary work has been carried out on the estimation of traces of copper by this reagent.

A mixed colour method has always been employed and a Spekker absorptiometer, with a 1-cm. cell and blue-green filters (Ilford 603).

(1) *Purification and storage of dithizone solutions*—The precipitation of dithizone (0·5 g.) from the ammoniacal extracts is always carried out by addition of a strong solution of sulphur dioxide. The latter is added to the combined ammoniacal extracts (after separation of impurities as described by Milton and Hoskins[12]) contained in a litre separating funnel, and the precipitated dithizone is shaken out with several small additions of chloroform (or carbon tetrachloride), the extract being run off each time into a 100-ml. volumetric flask used only for storing this reagent. The combined extracts are made up to the mark with the solvent used, covered with a small quantity of the strong sulphur dioxide solution (although Sandell[15] states that this procedure does not increase the stability of the solution) and stored in a refrigerator. Appropriate quantities are taken from this stock and diluted with the organic solvent just before use. The purified dithizone is never stored as the dry product after removal of the solvent. Hydrochloric acid is not used to precipitate the dithizone from the ammoniacal solution, for there is some evidence that, on occasions, it leads to erratic results in subsequent determinations.

(2) *Working conditions*—To obtain the best results with the Spekker absorptiometer it has been found necessary to use it in a dark room. Further, when using dilute dithizone solutions, the extraction of mercury is always carried out in a darkened room and the reading of transmittances taken as soon as possible after extraction (see, for example, Laug and Nelson[10]). It has never been found necessary to treat the dithizone extract with a dehydrating agent. A small roll of filter paper is inserted into the stem of the funnel and the extract run off slowly into the absorptiometer cell. The removal of excess dithizone by ammonia has been stated by Leibhafsky and Winslow[11] to be less satisfactory than a mixed colour method. There is a danger that with the more alkaline solutions some of the metal complex may be decomposed and under less alkaline conditions the dithizone may not be completely extracted. Further, the extra manipulation involved enhances the possibility of decomposition of the unstable mercury complex. In general, dithizonates are, however, more easily decomposed in carbon tetrachloride solutions. Excess dithizone is more easily removed from carbon tetrachloride solutions than from chloroform solutions, since the partition coefficient $Dz_{water}/Dz_{organic\ solvent}$ is greater for the former solvent at the *p*H values normally used (Clifford and Wichmann[4]). When an absorptiometer is available a mixed colour method would, in general, seem preferable.

(3) *Digestion*—If only small quantities of organic material are present, as in small paint samples, digestion with sulphuric acid followed by hydrogen peroxide (100 vol. M.A.R.) is satisfactory. After removal of excess of the latter with potassium permanganate the solution is treated with hydroxylamine hydrochloride and a direct mercury determination carried out on the solution thus obtained.

(4) *Extraction of copper and mercury by dithizone*—In their work, Milton and Hoskins[12] used chloroform solutions of dithizone; the marked contrast in the behaviour of chloroform and carbon tetrachloride solutions of the reagent with respect to the extraction of copper is to be stressed, since any method of separation of the two metals based on the relative rates of extraction is considerably affected by the solvent used. At low *p*H values the rate of extraction of copper by chloroform solutions of the reagent is very much slower than by a carbon tetrachloride solution. Thus, shaking a solution (100 ml.) containing 70 μg. of copper and 5·5 μg. of mercury at *p*H 1·2 for 1 minute with a chloroform solution of the reagent will only cause an error of 0·3 μg. in the mercury estimation. Quite large quantities of copper can be shaken with comparatively little extraction if the *p*H is kept low, as is indicated by Table I.

TABLE I

100 ML. OF SOLUTION; 10 ML. OF DITHIZONE IN CHLOROFORM; *p*H 1·4

"Spekker" set at 0·740 against pure chloroform.

Time of shaking, min.	0·6 mg. of copper Spekker reading (corrected)	1·5 mg. of copper Spekker reading (corrected)
1	0·706	0·646
2	0·671	0·589
4	0·641	0·523
8	0·526	0·374

At higher *p*H values the extraction is more rapid (Table II), although still much slower than the extraction of mercury.

TABLE II

100 ML. OF SOLUTION; 10 ML. OF DITHIZONE IN CHLOROFORM; *p*H 4·2

"Spekker" set at 0·740 against pure chloroform.

Time of shaking, min.	7·5 μg. copper Spekker reading (corrected)
1	0·660
2	0·587
4	0·517
10	0·506
15	0·500

The figures in Table III illustrate the rapidity of extraction of mercury even at low *p*H values.

TABLE III

100 ML. OF SOLUTION; 10 ML. OF DITHIZONE IN CHLOROFORM; *p*H 1·4

"Spekker" set at 0·740 against pure chloroform.

Time of shaking, min.	5·5 μg. of mercury Spekker reading (corrected)
1	0·603
2	0·608
4	0·605
10	0·608

In contrast, even at low *p*H values (Table IV), the copper is rapidly extracted by a carbon tetrachloride solution of the reagent and at a higher *p*H values still more rapidly.

TABLE IV

100 ML. OF SOLUTION; 10 ML. OF DITHIZONE IN CARBON TETRACHLORIDE; *p*H 1·16

"Spekker" set at 0·740 against pure carbon tetrachloride.

Time of shaking, min.	5·2 μg. of copper Spekker reading (corrected)	2·6 μg. of copper Spekker reading (corrected)
1	0·630	0·705
2	0·616	0·670
5	0·598	0·671

With certain metals, including bivalent copper and mercury, dithizone combines to form keto- and enol-metal derivatives of the type XDz_2 and XDz, respectively. The former are obtained in acid or neutral solutions and the latter in basic solutions or with a large deficiency of dithizone. The relations are clearly complex and there are few data on which to base theoretical deductions, although a simple case in which equilibrium was established has been treated in some detail by Kolthoff and Sandell,[9] (see also Wichmann[17]). Even less is known about the rates of the reactions concerned than the equilibrium constants. (For recent work on the formation of metal complexes, see Calvin and Wilson.[3]) The marked effect of *p*H may be taken to indicate that the reaction between metal and dithizone takes place in the aqueous phase, and it may be assumed that partition equilibrium between the aqueous and organic solvent phases is rapidly established on vigorous shaking for both dithizone and metal dithizonates. The rate at which metal dithizonate is brought into the organic solvent will therefore depend on the rate of production of the appropriate form of dithizone in the aqueous phase and the rate of reaction with the metallic ion concerned.

From the analytical standpoint, in the separation of copper and mercury the relative rates of transference may be of more practical importance than the equilibrium values, for the latter may not be attained under normal working conditions: this is particularly so when working at low *p*H values with chloroform solutions of the reagent.

Greenleaf[5] states that copper is readily extracted by a carbon tetrachloride solution of dithizone at *p*H 2, and Sandell[14] that it is completely extracted by 30 to 45 seconds vigorous shaking with the same reagent (3 to 20 μg. of copper in 25 ml. of sample). However, the latter investigator, using an extraction technique and a working curve based on pure copper solutions, found an incomplete recovery of added copper. The same author, in a later publication,[15] recommends shaking the solution to be extracted for 2 minutes. Sherman and

McHargue[16] point out that extraction of copper as well as zinc proceeds more slowly than is usually stated in the literature, whilst the slow rate of extraction in acid solution and the greater ease of extraction of zinc with carbon tetrachloride solutions has been noted by Hibbard.[7,8]

This work was carried out by the author when Investigator to the Marine Corrosion Sub-Committee of the Iron and Steel Institute.

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THE MARINE STATION
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Determination of Small Quantities of Manganese in Caustic Soda

BY C. G. ETHRINGTON AND J. W. HUGHES

A METHOD was required for the estimation of quantities of manganese of the order of 0·03 parts per million, in the routine examination of commercial caustic soda samples.

The most commonly known methods for the estimation of manganese have been those utilising bismuthate or persulphate,[1,2] though four reagents are described by Vogel,[3] who refers to potassium persulphate as widely used but unsatisfactory owing to the incompleteness of reaction, and potassium periodate as the most satisfactory but subject to limitations in respect of manganese, chlorine and iron contents. Two methods[4] have been suggested recently for the estimation of manganese in caustic soda solutions, but they were not considered suitable for rapid accurate routine tests; a later method[5] was developed, but was not applicable to our particular requirements owing to the concentration of salts that would be present after the necessary neutralisation of the sodium hydroxide.

In the past, use has been made of flocculent precipitates for collecting small amounts of finely dispersed metals in solutions.[6] Attempts were therefore made to separate small quantities of manganese from caustic soda solutions by co-precipitation with magnesium hydroxide and to estimate their amount by a persulphate or periodate method.

This method was tried on 300-ml. portions of a 20 per cent. sodium hydroxide solution, to which had been added known amounts of a standard solution of manganous sulphate (1 ml. $\equiv 3{\cdot}078 \times 10^{-6}$ g. of Mn). The manganese was then "extracted" as follows. To 15 ml. of a 10 per cent. solution of $MgSO_4.7H_2O$ was added a little of the sodium hydroxide solution, the mixture was shaken to a thin cream, and then the remainder of the 300 ml. was added, and the mixture poured into a cylinder, with maximum stirring effect, to ensure distribution of the magnesium hydroxide; after standing overnight at room temperature, the supernatant liquor was syphoned off, and the residual "mud" was taken as containing the magnesium and manganese.

The first attempts to estimate the manganese in the mud were made with ammonium persulphate. Several variations on the method were applied,[1,3,7,8] but this reagent was later regarded as unsatisfactory because the results were not always reproducible, the permanganic colour being unstable and often affected by a brown tint; moreover, the manipulation was lengthy, owing mainly to the necessity for removal of chlorides as silver chloride, by filtration.

Nevertheless, there was every indication that the full manganese content of the soda samples was being removed by the precipitation of the magnesium. The use of persulphate was discontinued and the periodate method was developed in conjunction with the collection of the manganese on precipitated magnesium hydroxide.

The preparation of the sodium hydroxide solutions and the precipitation and settling of the magnesium hydroxide were carried out as before. The supernatant liquor was siphoned off, leaving a total volume of "mud" and clear liquor of 40 ml. This was transferred to a 200-ml. tall-form pyrex beaker and to it was added 0·1 g. of $Na_2SO_3.7H_2O$, followed by 20 ml. of diluted sulphuric acid (1 + 1). The acidified solution was boiled for 15 minutes to remove all traces of sulphur dioxide, which would produce a brown colour on the subsequent addition of periodate. Five ml. of syrupy phosphoric acid were next added and then 0·1 g. of potassium periodate and the solution was boiled for 15 minutes. (The colour was slow to develop and it was necessary to boil for at least 5 minutes after the appearance of a pink coloration.) The solution was transferred to a Nessler glass and matched after 5 minutes against 0·001 *N* potassium permanganate in a second Nessler glass containing 5 per cent. phosphoric acid solution which had been treated with periodate. The 0·001 *N* permanganate was freshly prepared from 0·1 *N* solution. A blank determination on caustic soda without addition of manganese was made with each test, in order to allow for the manganese content of the reagents. Results are shown in Table I.

TABLE I

Std. $MnSO_4$ soln. added, ml.	Equivalent Mn, g. × 10^{-5}	0·001 *N* $KMnO_4$, ml. Total	Blank	Nett	Equivalent Mn, g. × 10^{-5}	Error %
6·0	1·85	2·60	0·80	1·80	1·98	+ 7·0
6·0	1·85	2·60	0·80	1·80	1·98	+ 7·0
6·0	1·85	2·85	1·20	1·65	1·81	− 2·2
6·0	1·85	2·85	1·20	1·65	1·81	− 2·2
7·0	2·15	3·00	1·00	2·00	2·20	+ 2·3
7·0	2·15	3·10	1·00	2·10	2·31	+ 7·4

In this series of tests no difficulty was experienced in matching the colours with 0·001 *N* permanganate.

Working on the assumption that the periodate method as outlined above was reasonably satisfactory, magnesium sulphate was added to sodium hydroxide solutions of various concentrations in order to determine suitable conditions for rapid settling; it was decided that a strength of approximately 10 per cent. of sodium hydroxide would give good settling of the magnesium hydroxide in 1 hour at room temperature, without involving undue dilution and increase in bulk.

The complete procedure adopted for the collection and estimation of manganese in caustic soda samples is as follows.

METHOD

Dilute the appropriate quantity of the caustic soda sample to about 10 per cent. concentration with distilled water. Put 15 ml. of a 10 per cent. solution of $MgSO_4.7H_2O$ in a tall cylinder (*e.g.*, of 500-ml. capacity, but dependent on the volume of sample solution required for a satisfactory estimation), add a little of the 10 per cent. sample solution, mix to a cream and then add the whole of the remaining sample solution, pouring from one cylinder to another to ensure good distribution of the magnesium hydroxide. Allow to settle for 1 hour and then siphon off the supernatant liquor, leaving 45 to 50 ml. of "mud" and liquor. Add to this 0·1 g. of $Na_2SO_3.7H_2O$ and 25 ml. of diluted phosphoric acid (1 + 1). Transfer the resulting clear solution to a 200-ml. tall beaker, rinsing the cylinder with water to give a final volume of about 120 ml. in the beaker, and cover this with a watch-glass. Boil the solution for 10 minutes to expel sulphur dioxide, add 0·4 g. of potassium periodate and boil for a further 10 minutes, adding water if necessary to maintain a volume of about 100 ml. Transfer the solution to a Nessler glass and after cooling for half an hour match it against standardised 0·001 *N* potassium permanganate by adding this to a Nessler glass containing 25 ml. of diluted phosphoric acid (1 + 1), 100 ml. of water and 0·4 g. of potassium periodate, previously boiled for 15 minutes.

Standardisation of the 0·001 *N potassium permanganate solution*—(i) Treat 6 ml. of standard manganous sulphate solution (1 ml. ≡ 3·078 × 10^{-6} g. of Mn) with 0·1 g. of $Na_2SO_3.7H_2O$, add 100 ml. of water and 10 ml. of diluted phosphoric acid (1 + 1), cover

with a watch-glass, and boil vigorously for 10 minutes. Then add 0·4 g. of potassium periodate and boil for 15 minutes, maintaining the volume at about 100 ml. Pour the solution into a Nessler glass (i).

(ii) Boil 10 ml. of diluted phosphoric acid (1 + 1), 100 ml. of water, and 0·4 g. of potassium periodate for 15 minutes, maintaining the volume at about 100 ml., and then pour into a Nessler glass. After half an hour add to this Nessler glass 0·001 *N* potassium permanganate sufficient to match the colour in Nessler glass (i).

In making the tests shown in Table II it was found that 1 ml. of permanganate solution (approximately 0·001 *N*) was equivalent to $1{\cdot}024 \times 10^{-5}$ g. of manganese.

No manganese was detected in the supernatant liquor from the samples containing up to 6 ml. of standard manganous sulphate solution. With 7 ml. and over, traces of manganese were found to be present, but in quantities too small for estimation by the accepted method.

TABLE II

Std. $MnSO_4$ soln. added, ml.	Equivalent Mn, g. $\times 10^{-5}$	$KMnO_4$ soln., ml. Total	Blank	Nett	Equivalent Mn, g. $\times 10^{-5}$	Error %
2·5	0·77	1·25	0·55	0·70	0·72	− 6·5
"	"	1·25	0·55	0·70	0·72	− 6·5
3·0	0·92	2·40	1·45	0·95	0·97	+ 5·4
"	"	2·05	1·20	0·85	0·87	− 5·4
"	"	1·40	0·55	0·85	0·87	− 5·4
"	"	1·55	0·65	0·90	0·92	nil
"	"	1·55	0·65	0·90	0·92	nil
"	"	1·55	0·65	0·90	0·92	nil
"	"	1·55	0·65	0·90	0·92	nil
3·5	1·08	2·50	1·45	1·05	1·08	nil
"	"	2·50	1·50	1·00	1·02	− 5·55
"	"	2·25	1·20	1·05	1·08	nil
"	"	1·70	0·70	1·00	1·02	− 5·55
"	"	1·55	0·55	1·00	1·02	− 5·55
4·0	1·23	1·70	0·55	1·15	1·18	− 4·05
"	"	1·70	0·55	1·15	1·18	− 4·05
"	"	2·70	1·45	1·25	1·28	+ 4·05
"	"	2·70	1·50	1·20	1·23	nil
"	"	2·00	0·70	1·30	1·33	+ 8·1
5·0	1·54	2·95	1·45	1·50	1·54	< 1
"	"	3·00	1·50	1·50	1·54	< 1
"	"	2·65	1·20	1·45	1·48	− 3·9
"	"	2·25	0·70	1·55	1·59	+ 3·25
6·0	1·85	2·40	0·55	1·85	1·89	+ 2·2
"	"	2·40	0·55	1·85	1·89	+ 2·2
"	"	2·35	0·55	1·80	1·84	< 1
"	"	2·35	0·55	1·80	1·84	< 1
7·0	2·15	2·60	0·65	1·95	2·00	− 7·0
"	"	2·60	0·65	1·95	2·00	− 7·0
10·0	3·08	2·00	0·65	1·35	2·76	−10·4
"	"	2·05	0·65	1·40	2·87	− 6·8
"	"	2·10	0·70	1·40	2·87	− 6·8
"	"	1·95	0·60	1·35	2·76	−10·4
"	"	2·05	0·60	1·45	2·97	− 3·6
12·0	3·69	2·40	0·70	1·70	3·48	− 5·7
"	"	2·40	0·70	1·70	3·48	− 5·7
15·0	4·62	2·60	0·60	2·00	4·10	−11·2
"	"	2·80	0·60	2·20	4·50	− 2·4
"	"	2·90	0·70	2·20	4·50	− 2·2
"	"	2·70	0·70	2·00	4·10	−11·2

Note—In all the tests taking 10 ml. or more of standard manganous sulphate solution, the precipitated magnesium hydroxide, after settling, etc., was dissolved and diluted to 100 ml., of which 50 ml. were taken for the estimation.

Collection of manganese—That the method of collection by co-precipitation with magnesium hydroxide is satisfactory (within certain limits as laid down later) is borne out by the fact that manganese is not detectable in the liquor after one "extraction" with magnesium, and also by the good agreement between the quantities of manganese added to the soda samples and those found by the periodate method as described (see Table II).

Method of estimation—The periodate method as described was found satisfactory within the limits stated below. The colours developed were stable and remained so for at least 24 hours, there being no increase in depth of colour after half an hour from the time of oxidation.

Accuracy—Provided the permanganate solution (approximately 0·001 *N*) is standardised against standard manganese solution, the collection and estimation of the manganese is accurate to about ±7 per cent., within the limits of useful application of the method.

Limits—From Table II it appears that such an amount of caustic soda solution should be taken as will give a total manganese content of from 0·8 to 2·0 × 10^{-5} g.; less than 0·8 × 10^{-5} g. gives colours too pale, and more than 2·0 × 10^{-5} g. colours too deep for accurate matching.

For larger quantities of manganese the Spekker absorptiometer can be used with advantage, but it was found that with concentrations of manganese within the above limits the depth of colour produced under the conditions given above was too pale. It might be possible to use the instrument with a 20-cm. cell, but at the time of writing this model was not available.

Effect of chloride content—Sodium chloride solution was added to 6-ml. portions of the standard manganous sulphate solution to give chloride contents of 0·00001 and 0·0001 g. No detectable difference in tint was observed, and it was concluded that the chloride content of commercial caustic sodas would not interfere with the estimation of manganese.

SUMMARY—

A method is described for the estimation of very small quantities of manganese in commercial caustic soda, by collection on precipitated magnesium hydroxide and subsequent oxidation with periodate in phosphoric acid solution.

We wish to thank Messrs. Courtaulds Ltd. for permission to publish this paper, Mr. G. Hegan for advice and criticisms, and members of the Preston Laboratory Staff for help in testing the method on a routine basis.

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COURTAULDS LTD.
RED SCAR WORKS, PRESTON

March, 1947

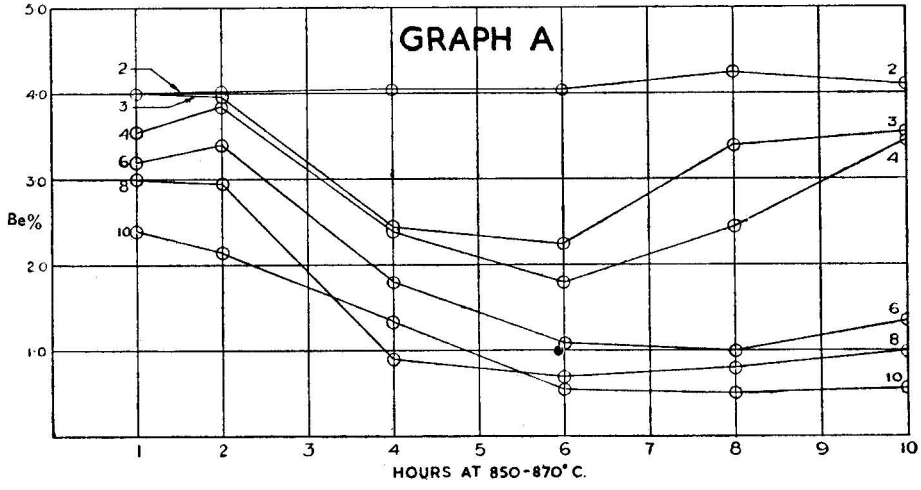
An Investigation into Factors affecting the Sodium Carbonate Fusion of Beryl

BY G. H. OSBORN

THE accurate determination of the beryllium content of beryl, $3BeO,Al_2O_3,6SiO_2$, has become of great commercial importance in recent years and considerable work, involving the use of *p*-nitrobenzene-azo-orcinol,[3] has been done on the subject by the author and Dr. W. Stross.[1,2] In these researches all the classical methods given for the attack on beryl, which is a very refractory material, were considered. It was found, surprisingly enough, that one of the most frequently recommended methods,[4,5,6,7] i.e., the sodium carbonate fusion, gave extractions so variable that attempts to use it were abandoned; a considerable amount of work had to be undertaken before a new and satisfactory method of attack by borax was found and published.[1]

Recently, however, the reason why such unsatisfactory extractions were obtained with the sodium carbonate fusion has been re-investigated by the author. On examining the literature it was found that whereas various ratios of sodium carbonate to beryl were given, most frequently 10 : 1, no details of temperature or time were mentioned, the direction frequently being to "fuse," without further amplification. It was therefore decided to carry

out a full investigation of times, ratios and temperatures. An electric furnace (Catterson Smith) was used, fitted with two carefully calibrated pyrometers, the leads of one of which were at the base, next to the crucible, and the leads of the other at the top of the furnace chamber. The pyrometers differed very little in their readings and were a good check on each other. The ratios of sodium carbonate to 1 of beryl taken were 2, 3, 4, 6, 10,* and three ranges of temperatures were examined, A, 850° to 870° C.; B, 1000° C. ±10°; C, 1200° C. ±20°. After fusion the melts were, in all cases, extracted with perchloric or sulphuric acid,



and the soluble beryllium contents determined by the *p*-nitrobenzene-azo-orcinol method.[1] The use of hydrochloric acid for extracting the melt was rejected owing to the very great risk of formation of the insoluble beryllium oxychloride, which would be removed with the silica and therefore lost. Hydrochloric acid has been recommended repeatedly for this purpose; the author carried out very many determinations with it, but did not once obtain a correct result, whereas with sulphuric or perchloric acid correct extractions were at all times obtained under suitable conditions. The beryl used was one that had been frequently assayed and found to have an average beryllium content of 4·3 per cent. It was ground to pass 150 mesh and intimately mixed with "AnalaR" sodium carbonate in platinum crucibles fitted with lids. All experiments in the same series were begun at the same time and the fusions were removed after the periods specified so as to have conditions as identical as possible.

The results obtained are shown in Graphs A, B and C, which relate to fusions at 850–870 °C., 1000° C. and 1200° C. respectively. The periods of fusion are shown along the abscissae, and the percentages of beryllium found along the ordinates. The number of each "curve" shows how many parts of sodium carbonate to 1 part of beryl were used in the fusions plotted on that particular "curve."

Experiment A (see Graph A)

It will be seen here that the ratio 2 : 1 gives an almost straight line throughout, whilst all the other ratios give very variable results. This is explained by the excess alkali producing the α-hydroxide of beryllium, which is gradually, but not completely, re-dissolved after prolonged heating. The lowest extraction was obtained at the most frequently recommended ratio 10 : 1.

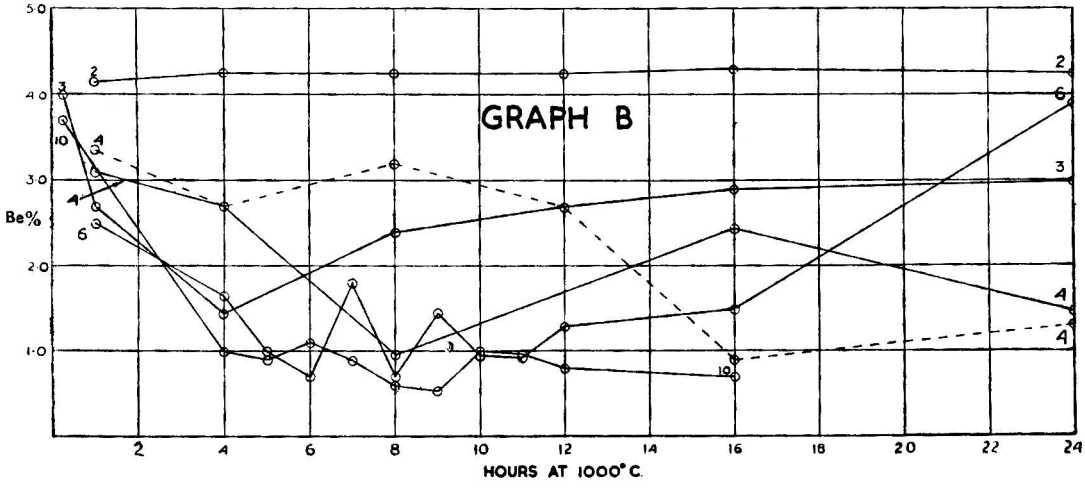
Experiment B (see Graph B)

Here again the 2 : 1 ratio alone gives a correct result, whereas the other ratios give results which are extremely variable. For reasons of space, the graph shows results only up to 24 hours, but the 3 : 1 and 4 : 1 series were extended for 48 hours without achieving a better extraction than 3 per cent. of beryllium. The 4 : 1 series was done in duplicate; one of the duplicate series is represented by a broken "curve," and it will be seen that with excess of sodium carbonate present no reproducibility can be assured, even under identical conditions.

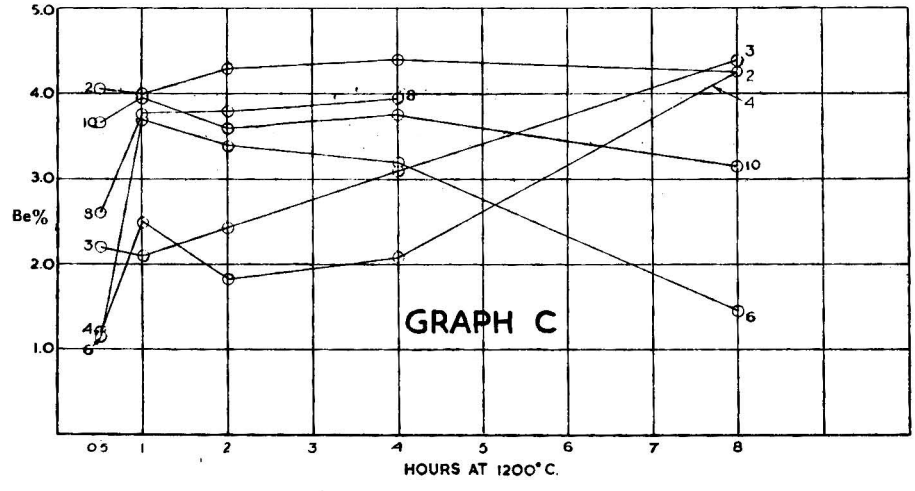
* The ratio 1 : 1 is not discussed here as it does not give complete extraction under any conditions, the quantity of alkali being insufficient.

Experiment C (see Graph C)

Here yet again the 2 : 1 ratio gives good results, and the other ratios give erratic results. The main difference from the previous experiments is that after 8 hours the effect of some of the ratios at this high temperature was to re-dissolve nearly all the α-hydroxide. This result could not, however, always be reproduced, whereas with the 2 : 1 ratio results were at all times reproducible.



Further examination of the literature showed that the insolubility of the α-hydroxide in sodium carbonate fusion was known, and attempts to utilise it were made,[8,9,10,11] but as these were based on total insolubility of the $Be(OH)_2$ it is not surprising that they were abandoned, for it may be clearly seen from the above graphs that even under the most carefully controlled conditions it is impossible to render all the beryllium insoluble. The real facts were, perhaps, better understood by the German workers, who based two patents[12,13] on the insolubility of the α-hydroxide in sodium carbonate. They attempted to use this



reaction to separate beryllium from the aluminium and silica in beryl. The beryllium was to be recovered by boiling the α-hydroxide in concentrated sulphuric acid. However, the fact that these patents were never worked, and that the inventor subsequently adopted the lime extraction on a large scale in Germany, would seem to indicate that it was not as successful as was claimed, and an examination of the graphs above shows that the difficulty of obtaining even an 80 per cent. extraction under these conditions is very great.

SUMMARY—A study has been made of the factors affecting the sodium carbonate fusion of beryl, *i.e.*, the time and temperature of fusion and the ratios of sodium carbonate to beryl, and it has been shown that (*a*) the high ratios of sodium carbonate to beryl frequently advocated are to be avoided owing to the formation and precipitation of the α-hydroxide, which is insoluble in acid and, therefore, lost with the silica when this is removed by filtration, and (*b*) the only ratio that has been found to give reliable results over all ranges of temperature from 800° to 1200° C., and over all periods of heating is 2 parts of sodium carbonate to 1 part of beryl. A convenient time of fusion for normal experimental work is half an hour.

Thanks are due to Mr. G. Abrey who carried out much of the experimental work under the author's direction, to Mrs. G. Stross who made most of the photometric measurements, to Dr. W. Stross for many fruitful discussions and valuable suggestions and to the Directors of International Alloys Limited, in whose laboratories these experiments were carried out, for permission to publish. Thanks are also due to Mr. Noel L. Allport, F.R.I.C., of The British Drug Houses Ltd., London, for helpful discussion and advice with the preparation of the manuscript, and to the author's colleagues at The British Drug Houses Ltd., B.D.H. Laboratory Chemicals Group, Poole, for assistance with the preparation of the graphs.

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CHURCH COTTAGE, IVINGHOE
NR. LEIGHTON BUZZARD, BEDS.

April, 1947

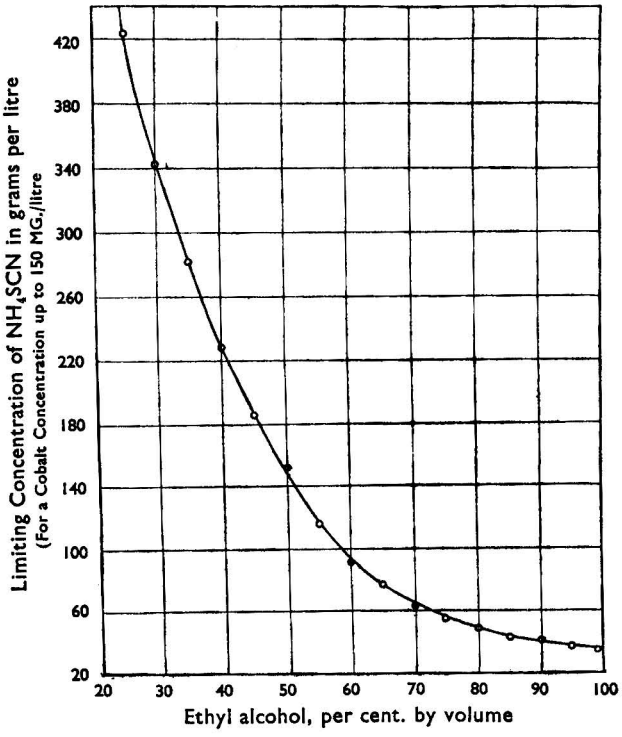
The Stability of the Cobaltous Thiocyanate Complex in Ethyl Alcohol-Water Mixtures and the Photometric Determination of Cobalt

BY NORBERT URI

TOMULA[1] was the first to propose the photometric determination of cobalt by means of its intensely blue thiocyanate complex. According to this method the cobalt is determined in a 50 per cent. (by volume) aqueous acetone solution containing 5 g. of ammonium thiocyanate per 100 ml., by comparing the extinction of this solution with that of a standard solution of similar cobalt concentration containing the same quantities of ammonium thiocyanate and acetone. As this method developed, special consideration was given to the disturbing effect of ferric ions: Kolthoff[2] proposes to remove them by transformation into the stable FeF_6''' complex; Ditz and Hellebrand[3] suggest their elimination by means of freshly precipitated calcium carbonate; Zemel,[4] for the analysis of sulphidic ores, proposes a mixture of sodium fluoride and sodium acetate; the use of pyrophosphate for the removal of iron and nickel is proposed by Lurie and Troitzkaja,[5] Lurie and Ginsburg,[6] and Zvenigorodskaya.[7] In all the investigations cited above, cobalt was determined according to Tomula's original procedure, in 50 per cent. aqueous acetone. Babicka[8] and Pevtsov,[9] on the other hand, suggest extraction of the blue $Co(SCN)_4''$ with a mixture of *iso*amyl alcohol and ethyl ether.

We investigated the stability of the cobaltous thiocyanate complex and worked out the conditions for the photometric determination of cobalt in mixtures of ethyl alcohol and water, and came to the conclusion that there was little if any advantage in the use of acetone over that of ethyl alcohol. The important point is that enough ammonium thiocyanate must be added, so that dissociation of the complex can be neglected. Under these conditions the colour intensity is the same when working with acetone or with ethyl alcohol.

Apparatus—The optical measurements were made with a Hellige Panphotometer. This apparatus is constructed on the principle of a visual abridged spectrophotometer with a movable light source. On one side, part of the light is absorbed by the sample solution (of constant layer depth), but on the other side—and in this the instrument differs from the Duboscq colorimeter—there is no standard solution. The intensity of the light reaching the two contiguous semi-circular fields of view of the ocular is equalised by moving the light



source nearer to or farther from the sample solution by means of a hand-wheel. The hand-wheel is fitted with a scale, calibrated in values of $\log_{10}(I_0/I)$, allowing the direct reading of the extinction of the sample solution. The apparatus is provided with filters for the spectral regions of 690, 660, 570, 550, 530, 500, 470, and 450 mμ. The extinction can be measured in a solution layer of 1, 5, 10, 20, or 50 mm.

EXPERIMENTAL—We measured the extinction of 0·0025 *M* cobaltous nitrate solutions at various concentrations of ammonium thiocyanate and ethyl alcohol. The extinction, measured at a constant cobalt concentration, depends on the concentrations of both ammonium thiocyanate and ethyl alcohol, but if, at constant alcohol content, the concentration of the thiocyanate is increased, a certain limiting concentration is reached beyond which any further increase does not measurably influence the extinction of the solution. At this limiting concentration we assume the formation of the complex to be practically complete, so that dissociation may be neglected. It was found that at and above the limiting concentration, which varies with the alcohol concentration, the extinction, when measured in the spectral region of 570 mμ., *i.e.*, in the proximity of the extinction maximum, was exactly proportional to the concentration of cobalt for concentrations up to 0·0025 *M*, *i.e.*, 147·4 mg. of cobalt per litre. No accurate proportionality was obtained at higher cobalt concentrations. The value of $\log_{10}(I_0/I)$ for a 1-mm. layer of a solution containing 147·4 mg. of cobalt per litre,

under the conditions of 100 per cent. thiocyanate complex formation, was found to be 0·280 in the spectral region of 570 mμ., corresponding to a molar extinction coefficient of 1120. Once the proportionality of the extinction with the concentration of the cobaltothiocyanate complex (up to ∿ 150 mg. of Co per litre) was established, it was easy to calculate, from extinction data at different concentrations of thiocyanate and ethyl alcohol, the degree of dissociation of the complex formed. (The colour of the cobaltous ion itself is altogether negligible at our working concentrations.) Thus we obtained a complete picture of the stability of the cobaltous thiocyanate complex in ethyl alcohol - water mixtures.

The results, in terms of percentage dissociation, are presented in Table I. Measurements were taken with an accuracy of ±1 per cent. For control purposes the extinction was measured immediately after the preparation of solutions and again after 24 hours, but the results obtained were the same. The graph in Fig. 1 shows the limiting concentration of ammonium thiocyanate in grams per litre over the entire range of ethyl alcohol - water mixtures. This graph should be taken into account in the analytical procedure. For concentrations of ethyl alcohol below 25 per cent. the limiting thiocyanate concentration exceeds the solubility of ammonium thiocyanate, and therefore accurate photometric determination is not practicable under these conditions. With alcohol concentrations above 25 per cent., however, the determination does give accurate results, provided the amount of thiocyanate added is not less than corresponds to the limiting concentration as shown in Fig. 1, and the cobalt concentration does not exceed about 150 mg. per litre. The extinction of the sample solution is compared with that of a standard solution of a cobalt salt which is determined gravimetrically. For the purpose of this investigation cobaltous nitrate solutions were determined electrolytically in presence of sodium citrate and acetic acid, according to a method developed by Spiegler[10] in these laboratories. It is not absolutely necessary that the cobalt concentration in the standard solution should be similar to that in the sample solution, provided it does not exceed 150 mg. per litre and the limiting concentration of ammonium thiocyanate is present.

TABLE I

DEGREE OF DISSOCIATION (IN PER CENT.) OF THE COBALTOTHIOCYANATE COMPLEX AT VARIED CONCENTRATIONS OF NH_4SCN IN ETHYL ALCOHOL - WATER MIXTURES

Cobalt concentration 0·0025 *M* corresponding to 147·4 mg. Co per litre.

Molar concentration of NH_4SCN	Vol. per cent. ethyl alcohol										
	0	10	20	30	40	50	60	70	80	90	99
5·0	85·2	71·5	43·5	0							
4·0	89·6	78·7	55·4	10·5	0			Complete			
3·0	95·2	87·6	66·2	23·2	0			complex			
2·0	100	95·5	83·0	55·8	12·7	0		formation			
1·5		100	91·0	74·5	26·2	12·5	0				
1·0		100	96·5	86·9	55·7	33·4	3·6	0			
0·75			100	92·5	72·5	46·4	12·5	4·5	0	0	
0·50			100	96·5	84·2	66·2	29·8	14·3	8·9	3·6	0
0·20				100	100	92·0	66·2	52·5	33·3	13·2	7·1
0·10		Complete				100	90·2	64·3	45·0	24·3	16·5
0·05		dissociation					100	90·0	75·2	58·3	33·0
0·02								100	97·5	88·3	70·5

Nickel forms a similar thiocyanate complex, which is (contrary to Tomula's assumption) no less stable than that of cobalt, as we proved by conductivity measurements; but its colour intensity is so weak in comparison with that of the cobaltous complex that we could determine cobalt (using the yellow-green 570 mμ. filter) under our working conditions in its presence up to a molar ratio 1 Co : 2 Ni without loss of accuracy. The colour intensity of the cobalt complex is so great that the metal can be determined at a concentration of only 0·5 mg. per litre in a solution layer of 50 mm.

Procedure—Pipette 1 ml. of the aqueous cobalt sample solution (at a maximum concentration of 1·5 g. per litre) into a 10-ml. volumetric flask, add 3 ml. of an alcoholic ammonium thiocyanate solution containing 150 g. per litre and dilute to the mark with 96 per cent. ethyl alcohol. Determine the extinction of this solution and compare it with that of a standard cobalt salt solution, preferably in the spectral region of 570 mμ. If for any of various reasons, such as the solubility of other substances present, the ethyl alcohol concentration must be

reduced (working minimum 25 per cent.), ascertain the amount of ammonium thiocyanate which is to be added from the graph in Fig. 1.

SUMMARY—

The stability of the cobaltous thiocyanate complex has been determined at various concentrations of ethyl alcohol and ammonium thiocyanate. The degree of dissociation of the complex was calculated on the basis of photometric extinction measurements. Conditions were worked out for the photocolorimetric determination of cobalt by the thiocyanate method in ethyl alcohol - water mixtures. It was found that there were limiting concentrations of ammonium thiocyanate, depending upon the ethyl alcohol concentration, above which the cobalt is practically quantitatively converted into a complex compound. Under these conditions Beer's law is obeyed, and the photometric determination gives accurate results.

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Notes

AN INDICATOR CHANGING AT *p*H 0·5 FOR THE CONTROL OF SULPHIDE PRECIPITATION

VARIOUS suggestions have been made for securing a complete and clear-cut precipitation of the metals of the hydrogen sulphide group. Treadwell insisted that the solution should be about 0·3 to 0·4 *N* in respect of hydrochloric acid, and some such figure as this is generally accepted. This value is usually obtained either by keeping some check on the amount of acid previously used and adjusting the volume accordingly, or by neutralising and then re-acidifying, or by some rapid method of titration.[1]

But these methods do not take into account either the small acidity produced by the hydrolysis of salts of weak bases or the buffering effects of salts of any weak acids that may be present. This buffering effect may be considerable; acetates, for instance, can completely spoil the separation.

If the usual theory of sulphide precipitation is accepted, some rapid method of controlling the concentration of $H^{\cdot}$ ions at between *p*H 0·4 and 0·5 is required. Fowles[2] suggests and uses methyl violet as an indicator for this *p*H. Given an experienced operator with a good eye for colour, this indicator can be used to show the correct hydrogen ion concentration. A more satisfactory indicator may be made by dissolving 0·3 g. of haematoxylin and 0·06 g. of methyl violet 6B in 100 ml. of 20 per cent. *iso*propyl alcohol. This indicator is golden yellow at *p*H 0·5, green at *p*H 1 and orange-red at *p*H 0.

Without some standard of comparison or some experience of its use, it is not very easy to decide when this indicator shows exactly *p*H 0·5, but it is usually sufficient to know that if the solution shows any greenish tint more acid is required, and that any orange tint indicates excessive acidity.

One complication occurs when basic salts such as those of antimony and tin are present. The haematoxylin is adsorbed on the basic precipitate and the colour of the adsorbed dye changes to a deep mauve, although the acidity of the solution may correspond to the green tint of the mixed indicator. In presence of these basic salts methyl violet alone is a useful indicator, and gives a grass-green tint at *p*H 0·5. The solution may not be quite clear at this acidity, but sulphide precipitation will be complete.

Trials with these indicators have shown their usefulness. A mixture of stannous chloride and copper and manganese sulphates, with the metal ion concentration corresponding to

0·05 *M*, was acidified, with methyl violet as indicator, and precipitated with hydrogen sulphide in the usual way. The filtrate, after the usual preliminaries, was concentrated and divided. One part was tested for traces of tin (after reduction) by the cacotheline reaction, and the other for copper with ferrocyanide. No trace of these metals could be detected. The precipitated sulphides were washed and examined by fusion with sodium carbonate and nitrate, but no manganese could be found. The whole experiment was repeated but with addition of enough sodium acetate to make the mixture 0·5 *M* in respect of this salt. Again precipitation of the copper and tin was complete, and no manganese was brought down. In each experiment manganese was subsequently precipitated from part of the filtrate in the ammonium sulphide group, and came down with an unusually clean appearance.

An interesting feature was that when the mixed indicator was used it coloured the Group III solution, despite boiling off the hydrogen sulphide and boiling with a little dilute nitric acid. Another solution was prepared, without the tin because of the haematoxylin complication, but with added aluminium. After adjustment of the acidity with the mixed indicator present, separation of the sulphides, and boiling and oxidising in the usual way, the aluminium came down in the ammonium hydroxide group characteristically coloured by the haematoxylin and leaving the solution colourless. The coloration of the precipitate greatly facilitated its detection when only a little was present.

In the separation of zinc from cadmium with use of this indicator it was found that, after precipitation from 0·05 *M* solutions of the metals and filtration from the sulphide precipitate, the filtrate was quite free from cadmium, so far as could be ascertained by concentration and spot-testing with diphenylcarbazide reagent, but the cadmium sulphide retained some zinc, which could not be removed by washing twelve times with boiling distilled water. When the zinc concentration was reduced to 0·01 *M*, cadmium sulphide still brought down a little zinc with it—enough to be detected with the mercuric ammonium cobalt thiocyanate reagent.* This is not necessarily a disadvantage, because an adequate quantity of zinc remains to be detected in the ammonium sulphide group. The explanation of the co-precipitation with cadmium is uncertain, but the possibility of the formation of a mixed salt as an alternative to adsorption must not be overlooked.

These experiments suggest that the use of a mixed indicator showing clearly when the *p*H of a solution is close to 0·5 is advantageous in improving the accurate separation of the Group II metals and also makes aluminium easier to detect. Certainly the indicator saves time.

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DETERMINATION OF CALCIUM OXIDE IN LOW-LIME REFRACTORY MAGNESIA

The oxalate - permanganate method outlined in a previous note[1] for the determination of lime in refractory dead-burned magnesia gives low results when less than 3 per cent. of lime is present. Although certain analysts[2] claim that amounts of calcium of this order cannot be satisfactorily determined by direct precipitation as oxalate, subsequent work has shown that the method can be modified to give accurate results down to a lime content of only 1 per cent.

Solutions corresponding to those obtained by dissolving magnesias containing 1 to 3 per cent. of lime in hydrochloric acid were prepared, and calcium was determined by carrying out two precipitations of calcium oxalate without removing iron and aluminium. Each solution (300 ml.) was heated, 50 g. of ammonium oxalate were added and dissolved with stirring, and after addition of methyl red solution calcium oxalate was precipitated at about 90 °C. by adding concentrated ammonia dropwise until the colour changed to yellow. The solution was maintained at about 90° C. for 60 minutes and then filtered hot. After washing with

* To the solution to be examined add an equal volume of a 0·02 per cent. aqueous solution of cobalt chloride followed by the same volume of an aqueous solution containing 2·7 per cent. of mercuric chloride and 3·0 per cent. of ammonium thiocyanate; the presence of zinc is indicated by formation of a blue crystalline precipitate.[3]

cold 0·1 per cent. ammonium oxalate solution the precipitate was dissolved in 20 ml. of hot dilute hydrochloric acid containing 5 ml. of the concentrated acid, 1 g. of ammonium oxalate was added and calcium oxalate reprecipitated in a volume of 250 ml. by dropwise addition of concentrated ammonia at the boiling point until the methyl red became yellow. The solution was gently boiled for 30 minutes and then set aside at room temperature for 1½ hours. The precipitate was washed with water and subsequently titrated with 0·1 *N* potassium permanganate. The results obtained are given in Table I.

TABLE I

Composition of solutions	CaO present g.	CaO found g.
	0, 0	0·0007, 0·0007
	0·0055, 0·0055	0·0034, 0·0034
0·995 g. MgO as $MgCl_2$	0·0055, 0·0055	0·0054, 0·0054
0·020 g. Fe_2O_3 as $FeCl_3$		
0·022 g. Al_2O_3 as $AlCl_3$	0·0110, 0·0110	0·0109, 0·0111
0 to 0·0329 g. CaO as $CaCl_2$	0·0110, 0·0110	0·0109, 0·0109
0·02 g. SiO_2		
5 ml. hydrochloric acid	0·0219, 0·0219	0·0225, 0·0225
Water to 300 ml.	0·0219, 0·0219	0·0223, 0·0223
	0·0329, 0·0329	0·0326, 0·0333
	0·0329, 0·0329	0·0330, 0·0329

When the lime present amounted to 0·0110 g. or more there was thus complete recovery. Similar results were obtained when the amount of ammonium oxalate used in the first precipitation was reduced to 25 g., but increasing the amount of hydrochloric acid used in this precipitation tended to produce low and varying figures.

Solutions were also prepared, corresponding to those obtained by alkali fusion of magnesias containing 1 to 3 per cent. of lime and subsequent solution of the melts in hydrochloric acid, and calcium was determined in them as above. Low figures were obtained with solutions containing less than about 0·02 g. of CaO, but it was found that correct results could be obtained with those containing only 0·01 g. of CaO, corresponding to a magnesia containing 1 per cent. of lime, if the first precipitation was made at the boiling point and the solution then gently boiled for 2 hours. Results obtained with this modification are given in Table II.

TABLE II

Composition of solutions	CaO present g.	CaO found (by titration) g.	CaO found (by weighing) g.
	0, 0	0·0006, 0·0006	
0·961 g. MgO as $MgCl_2$	0, 0		0, 0
0·020 g. Fe_2O_3 as $FeCl_3$			
0·021 g. Al_2O_3 as $AlCl_3$	0·0054, 0·0054	0·0043, 0·0045	
0 to 0·0323 g. CaO as $CaCl_2$	0·0053, 0·0053		0·0034, 0·0044
0·02 g. SiO_2			
5 ml. hydrochloric acid	0·0108, 0·0108	0·0107, 0·0109	
6 g. NaCl (≡5 g. Na_2CO_3)	0·0106, 0·0106		0·0102, 0·0110
Water to 300 ml.			
	0·0215, 0·0215	0·0219, 0·0221	
25 g. $(NH_4)_2C_2O_4.H_2O$ used in first precipitation	0·0213, 0·0213		0·0212, 0·0214
	0·0323, 0·0323	0·0329, 0·0331	
	0·0319, 0·0319		0·0320, 0·0320

Figures obtained by igniting the precipitate to calcium oxide agreed closely with those obtained by titration with permanganate.

On the basis of the above results the following procedure is recommended for the determination of lime in refractory magnesias containing from 1 to 3 per cent. of CaO.

PROCEDURE—

Grind the sample to pass a 200-mesh B.S.I. sieve, and dissolve 1 g. in hot dilute hydrochloric acid containing 10 ml. of the concentrated acid. Boil with a few drops of nitric acid to oxidise ferrous iron.

Dilute to 300 ml., heat, add 25 g. of ammonium oxalate and dissolve by stirring. Add methyl red solution, and precipitate calcium oxalate at about 90° C. by dropwise addition of concentrated ammonia until the colour changes to yellow. Maintain at about 90° C. for 60 minutes. Filter hot, and wash thoroughly with cold 0·1 per cent. ammonium oxalate solution. Dissolve the precipitate in 20 ml. of hot dilute hydrochloric acid, containing 5 ml. of the concentrated acid, and wash the filter paper with hot diluted hydrochloric acid (1 in 100).

Add 1 g. of ammonium oxalate, dilute to 250 ml., heat to boiling and precipitate calcium oxalate as above. Boil gently for 30 minutes, and then set aside at room temperature for 1½ hours. Filter, wash thoroughly with cold water, and titrate with 0·1 *N* potassium permanganate solution.

If the sample will not dissolve in hydrochloric acid, fuse 1 g. with 5 g. of anhydrous sodium carbonate and dissolve the cold melt in dilute hydrochloric acid containing 20 ml. of the concentrated acid. Boil with a few drops of nitric acid to oxidise ferrous iron.

Dilute to 300 ml., add 25 g. of ammonium oxalate and heat to the boiling point. Add methyl red solution and precipitate calcium oxalate by dropwise addition of concentrated ammonia until the colour changes to yellow. Boil gently for 2 hours, allow to cool slightly, and filter hot. Wash thoroughly with cold 0·1 per cent. ammonium oxalate solution, dissolve the precipitate in acid, carry out a second precipitation, and complete the determination as described above.

This procedure was tested on samples of two commercial refractory magnesias with the following results:—

Sample	CaO per cent. found by Solution in HCl	Alkali fusion	CaO per cent. found by another method
Dead-burned sea-water magnesia ..	1·97	1·95	1·95
Calcined Indian magnesite	1·08	1·11	1·03

Solution of the samples in hydrochloric acid gave almost the same results as fusion with sodium carbonate followed by solution in hydrochloric acid; this was to be expected, since both materials were found to be completely decomposed by hydrochloric acid. The actual lime content of each was determined by dissolving in acid, removing ferric oxide and alumina by two precipitations with ammonia, increasing the amount of lime present by adding standard calcium chloride solution, carrying out two precipitations of calcium oxalate and subsequently titrating with permanganate. It is well known that when the ratio of calcium to magnesium is not very small the oxalate separation is satisfactory, and the actual lime content was therefore obtained by subtracting the amount added as calcium chloride from the amount determined by titration. As can be seen, the actual amounts of lime present closely corresponded with those obtained by the method given under "Procedure."

I wish to thank the Research Manager and the Directors of the British Periclase Company for permission to publish this note.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Methods of Fat Determination in Dairy Products. L. C. Janse (*Chem. Weekblad*, 1946, **42**, 284–288)—A critical comparison of the three chief methods for fat determination has been made. *The Röse - Gottlieb method*—Results obtained by the Röse - Gottlieb method tend to be high, partly through oxidation of the fat by peroxides in the ether, and partly through extraction of non-fatty substances. *The Weibull method*—The official method of the Committee of the Dutch Dairy Association (*Off. Org. van Feder. Nederl. Zuivelfab.*, 1941, 569–570, 581–583, 594–596), modified in a few details by the author, is as follows. Transfer 25 g. of milk to a beaker, add a little pumice, and 50 ml. of 4·8 *N* hydrochloric acid. Cover with a clock glass, and boil gently for 20 min. Rinse down the clock glass with hot water, and pass the contents of the beaker through a wet and well-fitted, fat-free filter paper (11 cm. diameter, free from holes). After washing free from acid, dry the filter paper at 100° C. for 1 hr., a watch glass being placed under the tip of the filter to catch any molten fat running through. Transfer the filter paper to a glass extraction tube having a number of small holes in the bottom, support the paper on fat-free cotton-wool, and cover it with a layer of the wool. Rinse the funnel and watch glass with light petroleum (b.p. 40° to 60° C.), and extract the filter paper with the light petroleum in a continuous extraction apparatus for 4 hr. into a dried weighed flask. Dry the fat for 2 hr. at 102° to 105° C. and to constant weight (less than 2 mg. loss on 0·5 hr. further heating). Application of the method to other dairy products requires modifications in the preliminary acid treatment. For buttermilk, take double quantities of sample and 4·8 *N* acid. For cream, take 3 to 5 g. of sample, 40 ml. of water and 30 ml. of 25 per cent. hydrochloric acid. For cheese, take 3 g. of sample, 25 ml. of water and 30 ml. of 25 per cent. hydrochloric acid and boil for 1 hr. For full-cream milk powder take 2·5 g. of sample, 20 ml. of water and 30 ml. of 25 per cent. acid, and for skimmed-milk powder double quantities of each. For condensed milk, dilute to the concentration of fresh milk and treat like this. *The Gerber method*—The Committee concluded that two errors led to high results by this method. The first, due to neglecting the volume of the meniscus, is small. The second error runs parallel with the fat content of the milk, amounting to 1·9 per cent. of the amount found. It may be compensated by allowing a correction either by taking 10·79 ml. of milk in place of 11 ml., or by multiplying the result by 0·981. This correction factor is a mean value, and agrees with the finding of an investigation by the author. G. M.

Puerto Rican Fatty Oils. VI. Characteristics and Composition of "Molinillo" Seed Oil. C. F. Asenjo, J. A. Goyco, and Z. Martinez-Pico (*J. Amer. Chem. Soc.*, 1945, **67**, 1936–1937)—The "molinillo," known also as lion's ears, "quina de pasto" and "botón de cadeta," is a mint plant (*Leonotis nepetæfolia* L.) growing abundantly as a weed in Puerto Rico. Its oil had the following characteristics: sp.gr. 25/25, 0·8984; n^{20}, 1·4673; iodine value (Hanus), 82·5; saponification value, 191·2; acid value, 11·20; Reichert - Meissl value, 0·29; Polenske value, 0·15; unsaponifiable matter, 3·09 per cent.; acetyl value, 4·87. The percentages of fatty acids and their glycerides, respectively, were: linoleic, 11·9, 12·4; oleic, 64·6, 67·6; myristic, 1·3, 1·4; palmitic, 12·0, 12·6; stearic, 1·2, 1·3. E. B. D.

Limit Tests for Impurities. F. Reimers and K. R. Gottlieb (*Contributions from the Danish Pharmacopoeia Commission. Vol. I. Ejnar Munksgaard, Copenhagen*, 1946)—It is not possible to abstract all the information contained in this publication (*cf.* review, p. 500), but some of the more interesting points may be noted. *Chloride*—Rapid mixing is essential to obtain a reproducible turbidity, and the solution under test should be poured all at once into the 0·1 *N* silver nitrate solution. Salts have little effect on the sensitivity, but nitric acid should be present in salt-free solutions. *Sulphate*—To obtain reproducibility, the reaction mixture must be "seeded" with barium sulphate. One drop of sulphate solution (100 μg. per ml.) is placed at the bottom of a test tube, and 1 ml. of 0·5 *N* barium chloride solution is added, with shaking. After 1 min., 10 ml. of the solution under test are added and the mixture is shaken violently for 10 sec. The comparison is made after 5 min. *Calcium*—"Seeding" with calcium oxalate is also to be recommended here. *Heavy metals*—Various factors affect the colours in a different way for different metals. The dithizone reagent is less suitable than sodium sulphide for a limit test, partly because the sensitivity is too high, but also because the colours of the complexes with different metals vary greatly. *Ammonia*—The solution under test, mixed with an equal volume of sodium hydroxide solution, is placed in a test tube. In the mouth of the tube is suspended, on a glass hook, a piece of red litmus paper. After heating in a water-bath for 5 min., the colour of the litmus paper is compared with that of a test paper treated similarly with standard ammonia solution. *Carbonates*—This test is similar to that for ammonia. The carbonate is decomposed by acid, and the test paper used is filter paper moistened with a mixture of 0·05 *N* sodium hydroxide and phenolphthalein.

Colour standards—Cobalt, iron, and copper solutions similar to those of the United States Pharmacopoeia are used, but all dilutions are made with acid so that the hue is not changed by dilution. *Limits*—In addition to the ordinary limit test ("Limit A"), if it is prescribed that a substance must not show any reaction for an impurity then the comparative control known as "Limit B" must be used. An example of the thoroughness of the tests is shown by the proposed monograph for distilled water: From 500 ml. of distilled water, 100 ml. of water are distilled off in a glass apparatus connected by means of ground-glass joints. These 100 ml. are denoted as P_2. Subsequently, another 300 ml. are distilled. The non-distilled residue is denoted as P_1. In the tests for colour, sulphate, calcium, and metals, the tests are performed on P_1, whilst P_2 is used for the controls. In addition, there are tests for carbon dioxide, reaction to methyl red, reducing substances, chloride, nitrate, sodium, ammonia, and non-volatile matter. G. M.

Assay for Choline Chloride in Pharmaceutical Products. W. C. Gakenheimer and R. M. Regnera (*J. Amer. Pharm. Assoc., Sci. Ed.*, 1946, **35**, 311–312)—The recent interest in the oral administration of choline for the treatment of certain diseases of the liver (Brown and Muether, *J. Amer. Med. Assoc.*, 1942, **118**, 1403; Russakoff and Blumberg, *Ann. Internat. Med.*, 1944, **21**, 848; Richardson and Suffern, *Brit. Med. J.*, 1945, i, 156) has indicated the need for an accurate assay of choline chloride in pharmaceuticals. The use of phosphotungstic acid as a precipitant has been found to be rapid and trustworthy.

Procedure—(*a*) *For liquid samples* (*solutions in water, elixirs, syrups, etc.*)—Transfer such a volume of the sample as might be expected to contain about 1 g. of choline chloride to a 100-ml. volumetric flask and heat on a steam-bath at reduced pressure (100 to 125 mm. of mercury) to drive off moisture and any interfering decomposition products such as ethylamine, if present. While it is still warm, shake the residue with 50 ml. of absolute alcohol, and dilute to 100 ml. with the same solvent. Mix thoroughly, allow to settle, transfer 5 ml. of the clear, supernatant fluid to a beaker containing 10 ml. of a filtered, 10 per cent. solution of phosphotungstic acid in absolute alcohol, digest the mixture on a steam-bath for 5 min. and filter through a fine-porosity, sintered-glass crucible. Wash the residue on the filter with 5 ml. of absolute alcohol, dry at 55° C. for 2 hr., and weigh.

Weight of precipitate × 0·1375 = weight of choline chloride.

(*b*) *For solid samples* (*tablets, capsules, etc.*)—Extract an accurately weighed portion, expected to contain about 0·5 g. of choline chloride, in a micro-Soxhlet apparatus with 20 ml. of absolute alcohol for 3 hr. Transfer the extract quantitatively to a 50-ml. volumetric flask, distil off the alcohol, and heat the residue at 100° C. under reduced pressure (100 to 125 mm. of mercury) for 15 min. Dissolve in absolute alcohol, dilute to 50 ml., and continue the assay as described above.

The factor, 0·1375, for converting the weight of choline phosphotungstate to choline chloride is higher than the theoretical figure of 0·1291 to compensate for the slight solubility of the phosphotungstate in absolute alcohol under the assay conditions described. Different batches of phosphotungstic acid have been examined under the same conditions; the weights of precipitate obtained varied by only ±0·7 per cent. It is stated that although pure, anhydrous alcohol was used in the experiments, anhydrous, denatured alcohol is satisfactory. It is advisable to conduct a blank determination to establish the absence of interfering substances in the preparation under examination; no such source of error has been encountered in several common vehicles tested. A satisfactory recovery of choline chloride is obtained. J. A.

Biochemical

Step-Photometric Determination of Histidine. K. Schmid (*Helv. Chim. Acta*, 1946, **29**, 226–228)—The method, which can be used to determine histidine in impure solutions, such as urine, is a modification of that of Kapeller - Adler (*Biochem. Z.*, 1933, **264**, 131) in which a slight excess of bromine is added to the histidine-containing solution and the resulting dye is developed by means of an ammonia - ammonium carbonate mixture, and determined photometrically. In the present method, the excess of bromine is removed by addition of arsenious acid (Conrad and Berg, *J. Biol. Chem.*, 1937, **117**, 350), the urine is strongly diluted before test, and the bromination is carried out in presence of an excess of acid.

Procedure—Dilute 24-hr. rat urine to 100 ml. with water. Treat 1-ml. portions of this diluted urine with increasing volumes of a histidine solution containing 100 mg. of histidine and 2 ml. of 2 *N* sulphuric acid per 100 ml. Also, prepare 0·04 *N* sulphuric acid and use this to dilute to 2 ml. urine samples containing histidine. Add dropwise a solution containing 2·5 ml. of bromine, 250 ml. of glacial acetic acid, and 750 ml. of water, until the slight yellow colour of the liquid after 10 min. standing shows that there is a slight excess of bromine present. After 10 min., add 2 drops of 10 per cent. aqueous ammonia solution saturated with arsenious acid and 2 ml. of an ammonia - ammonium carbonate solution (2 parts of concentrated ammonia + 1 part of 19 per cent. ammonium carbonate solution). Heat in boiling water for 5 min., cool, and allow to stand at room

temperature for 10 min. to develop the colour. Dilute to 10 ml. with the ammonia - ammonium carbonate solution, and determine the intensity of the colour with a step-photometer, using an S50 filter and a 5-mm. cell. As the compensating liquid use urine treated in the same way. For 0·4 to 1·6 mg. of histidine hydrochloride per millilitre in the diluted urine there is a linear relationship between the histidine content and the extinction.

The method is ten times less sensitive than that of Edlbacher *et al.* (*Z. physiol. Chem.*, 1941, **270**, 158), but has the advantage of being specific for histidine. E. M. P.

Method for the Estimation of Barbituric and Thiobarbituric Acids in Biological Materials. J. Raventos (*Brit. J. Pharmacol.*, 1946, **1**, 210–214)—In order to study the fate and distribution of barbiturates in the animal body, several methods of estimation were examined, but none was completely satisfactory. Using the methods of Levvy (*Biochem. J.*, 1940, **34**, 73), Delmonico (*Proc. Mayo Clin.*, 1939, **14**, 113), and Anderson and Essex (*Anaesthesiology*, 1943, **4**, 113) the recoveries of known amounts of barbiturates added to blood or tissues were low. A method was developed for the estimation of barbituric acid based upon Koppanyi's colour reaction (*J. Amer. Pharm. Assoc.*, 1934, **22**, 1076), and for the estimation of thiobarbituric acids on a colour reaction described by Cowan.

Procedure—A. *Extraction*—Using blood, take 10 to 20-ml. volumes of oxalated blood and mix with equal volumes of water and of a 10 per cent. solution of sodium dihydrogen phosphate. Extract with ether in a continuous extractor at 45° to 50° C. for 8 to 10 hr. Evaporate the ether extract to dryness. For urine, acidify to *p*H 5 with concentrated hydrochloric acid and extract with ether in a similar manner. When using tissues, take samples of 10 to 20 g., grind in a mortar with sand, and then mix with 10 per cent. of solid sodium dihydrogen phosphate. Allow to stand for 5 to 10 min., add 20 g. of anhydrous sodium sulphate for every 10 g. of tissue with continuous grinding. Transfer to a desiccator containing calcium chloride for one hr. Extract the dry powder for 2 to 3 hr. with 50 ml. of benzene in a well-stoppered flask. Filter and wash three times with 10 to 15 ml. of benzene. Concentrate the filtrate and washings to about 5 ml. by distillation at 50° C. under reduced pressure.

B. *The separation of barbituric and thiobarbituric acids*—The extracts must first be purified by chromatography. Dissolve the residues obtained from the extraction of urine or blood in 5 ml. of chloroform and dry with 1 to 2 g. of anhydrous sodium sulphate. Add the solutions to columns of activated alumina $\frac{3}{8}$ in. × 4 in. The activated alumina used was grade O supplied by Messrs. Peter Spence of Manchester, and was treated by boiling 1200 g. with 1800 ml. of 10 per cent. acetic acid for 2 hr., filtering and washing with at least 20 litres of hot, distilled water. The alumina was dried, heated until the temperature reached 360° C., and then partly de-activated by adding $2\frac{1}{2}$ per cent. w/v of water. Filter the chloroform solutions on to the columns and wash the flask and filter 3 times with 5 ml. of chloroform, pouring the washings on to the column. Wash the column with chloroform until the eluate is free from pigment. When tissues are used, pass the benzene extract through alumina columns with slight suction, washing the flasks with benzene and using benzene to elute the pigment from the columns, and finishing with 20 ml. of chloroform. The chloroform and benzene washings are discarded. Thiobarbituric acids are recovered from the columns by elution with 50 ml. of 2 per cent. methanol in chloroform, the eluates being kept for estimation. To elute the barbituric acids, use 50 ml. of 10 per cent. methanol in chloroform. Under these conditions separation is complete, and the recoveries of both acids are almost theoretical.

C. *Estimation*—Evaporate the eluates to dryness under reduced pressure at 40° to 50° C. and dissolve the residues in chloroform.

Thiobarbituric acids—Take an aliquot of the final chloroform solution in a test tube, and for every 2 ml. add 0·2 ml. of a 10 per cent. solution of diethylamine in methanol followed by 0·5 ml. of a saturated solution of anhydrous copper sulphate in methanol. A green colour develops at once and is stable for about 2 hr. Compare the samples in a suitable colorimeter with a series of similarly treated standard solutions of the thiobarbituric acid to be estimated, containing 0·03 to 0·5 mg. per ml. Tissues such as brain and liver give a blank value sometimes as high as 1 mg. per 100 g. of tissue. The reaction is fairly selective, not being given by malonic acid, theophylline, theobromine, thiourea, caffeine, guanine, uric acid, urea, creatinine, oxamide, succinic acid, lecithin, cholesterol, cystine, or glutathione.

Barbituric acids—For every 2 ml. of the final chloroform solution add 0·6 ml. of 5 per cent. *iso*propylamine in methanol followed by 0·1 ml. of a 1 per cent. solution of cobalt acetate in methanol. A reddish colour is produced and can be compared in a colorimeter with a series of similarly treated standards containing 0·1 to 1 mg. of the appropriate barbituric acid per ml. of chloroform. The recovery of known amounts of barbituric or thiobarbituric acids added to blood and tissues is approximately complete except when the amount from a 10-ml. sample is less than 0·3 mg.; recovery may then fall below 95 per cent. R. H. T.

Chemical Assay of Penicillin. M. Mundell, H. Fischbach, and T. E. Eble (*J. Amer. Pharm. Assoc., Sci. Ed.*, **1946**, **35**, 373–378)—Methods for the assay of penicillin are reviewed, and the occurrence of the four types of penicillins G, K, F, and X, is pointed out. Data are given of the relative activities of these substances against *Staphylococcus aureus in vitro*. The following chemical methods were investigated:—the colorimetric method of Scudi (*J. Biol. Chem.*, 1946, **164**, 183), the penicillinase method (Murtaugh and Levy, *J. Amer. Chem. Soc.*, 1945, **67**, 1042), the methods proposed by the Chas. Pfizer Co. based upon alkali inactivation and hydrogen peroxide inactivation, a spectrophotometric method (Herriott, *J. Biol. Chem.*, 1946, **164**, 725), and the iodimetric method proposed by the Squibb Institute for Medical Research (Alicino, *Ind. Eng. Chem., Anal. Ed.*, **1946**, **18**, 619; *Abst.*, ANALYST, **1947**, **72**, 68).

It was found that the penicillinase method and the iodimetric method gave the most consistent results when applied to diverse samples of commercial penicillin. The paper describes both methods in full, but points out that the iodimetric method gives better results generally and is technically simpler and more straightforward. The authors examined the factors involved in the iodimetric reaction of the alkaline products of inactivation of sodium penicillin G and found that 2·52 to 2·53 ml. of 0·01 *N* iodine are consumed by the inactivation product from 1 mg. of crystalline sodium penicillin G. The following method is proposed for the assay of ampoules of penicillin.

Procedure.—Place 5-ml. aliquots of a solution of penicillin (approximately 1000 units/ml.) in each of two iodine flasks. To one, add an equal volume of *N* sodium hydroxide and allow to stand at room temperature for 15 min. and then add 5 ml. of 1·1 *N* hydrochloric acid and 15 ml. of 0·01 *N* iodine. After 15 min., titrate the excess of iodine with 0·01 *N* sodium thiosulphate, approaching the end-point with the use of starch indicator and the addition of 5 ml. of carbon tetrachloride. To the second flask add 15 ml. of the 0·01 *N* iodine and titrate immediately to serve as a blank determination. The difference between the two titration values divided by 2·52 gives the number of milligrams of penicillin present. The use of the 1·1 *N* solution of hydrochloric acid results in a medium of low *p*H which has been shown to be advantageous for iodimetric titrations. No adjustment of *p*H is made to the blank determination since this would result in the formation of degradation products that would react with iodine and yield correspondly low value for the penicillin potency.

A series of batches of sodium penicillin G was assayed by this procedure and recoveries ranging from 99 to 101·6 per cent. of the theoretical were obtained. A few samples of penicillins F, X, and K were assayed both by the iodimetric and penicillinase methods, and the results indicate that a similar number of equivalents of iodine react with equimolecular quantities of the respective penicilliates resulting from alkaline inactivation. The work of the Squibb group suggested that penicillin X might give abnormally high values, but the results obtained did not show this. Comparative data obtained for samples of crystalline penicillin G using the iodimetric, penicillinase, and bio-assay methods are given. The results show good agreements between the chemical methods, the average recoveries being 99·8 per cent. for the penicillinase, 99·2 per cent. for the iodimetric, and 98·2 per cent. for the bio-assay method. The standard deviations from the known weight of penicillin were, respectively, 1·5 per cent., 1·2 per cent., and 4·8 per cent. Good agreement was similarly obtained with samples of commercial penicillin.

The results of the chemical methods are most accurately expressed in milligram-equivalent weights of penicillin without any reference to the type of penicillin involved. Since the molecular weights of the various known penicillins are of the same order, little error is to be anticipated by converting the results to milligrams by multiplying by the average of the molecular weights of the four penicillins. The results cannot be accurately translated to the unit basis without knowing the proportions of the four penicillins present. Hence, comparisons of the accuracy of the chemical and biological methods must be made upon material of known composition. The penicillinase method requires the use of special equipment, and is difficult to apply to some preparations of penicillin. It is probably safe to assume that it is highly specific, and methods based upon its action are specific for penicillin. The iodimetric method requires no special apparatus or reagents, and can be successfully applied to most preparations of penicillin, but is not specific for penicillin, so that in the absence of information on the composition of the sample, supplementary analysis might be required.

R. H. T.

Three-Hour "Physical Development" Cup-Plate Assay for Penicillin. F. M. Goyan, J. Dufrenoy, L. A. Strait, R. Pratt, and J. Juntunen (*J. Amer. Pharm. Assoc., Sci. Ed.*, **1947**, **36**, 65–68)—A practical method for the assay of penicillin depending on the fact that cells of *Staphylococcus aureus* differ in their affinity for silver, supplied in the form of an aqueous solution of silver nitrate, according to whether they are under the influence of penicillin or not, is described. It has been found that the silver-impregnated plates are analogous to photographic emulsions, and the application of principles of photographic development produces images that show a marked difference

between zones of inhibition and non-inhibition with a clearly defined boundary between the zones after only 5 hr. incubation. If the seeded plates are incubated for 3 hr. before the beginning of the assay, satisfactory images are produced after only 3 hr. incubation, and normal results have been obtained using such "pre-incubated" plates after storage for 5 days in a refrigerator.

Procedure—Prepare and seed the plates as for the standard cup-plate method of assay of penicillin, using *Staph. aureus*, NRRL Strain No. 313 (F.D.A. Strain No. 209P), incubate at 38° C., and store in a refrigerator until needed. Transfer the solutions to be tested to cylinders on the plates in the usual manner and re-incubate at 38° C. for 3 hr. After removal from the incubator, flood each plate with about 30 ml. of a nearly neutral, 0·1 per cent. aqueous solution of silver nitrate, expose for 2·5 to 3 min. to the illumination from two 40-watt daylight fluorescent lamps mounted in a reflector at a distance of about 35 cm. (this is equivalent to about 350 foot-candles). Remove the excess of silver nitrate solution by means of a suction device and then add 30 ml. of physical developer prepared as described below. After allowing the developer to act for 7 to 10 min., measure the diameters of the zones of inhibition in the conventional way.

Preparation of Physical Developer. Stock Solution A—Dissolve 80 g. of sodium thiosulphate and 20 g. of anhydrous sodium sulphite in 300 ml. of distilled water and add to this solution, slowly with constant stirring, a solution of 8 g. of silver nitrate in 200 ml. of distilled water. *Stock Solution B*—Dissolve 20 g. of sodium sulphite in 500 ml. of distilled water and, when dissolution is complete, add 3·8 g. of 2 : 4-diaminophenol hydrochloride and stir until dissolved. Store both stock solutions in a refrigerator and, just before use, mix equal volumes of solutions *A* and *B* and dilute their combined volume with 3 volumes of distilled water. The dilution of the developer and the time of development should be determined empirically for each laboratory, to allow for varying conditions of light intensity, temperature of development, etc. The concentration of silver nitrate used for impregnating the plates must be not less than 0·1 per cent. nor greater than 0·13 per cent., whilst the time of exposure must be adjusted empirically, as is customary in adjusting the time of exposure of photographic materials. The curve relating concentration of penicillin with diameters of zones of inhibition is linear from 1·0 unit per ml. to 8·0 units per ml. when plotted on log-log paper. Figures indicating that penicillins of varying degrees of purity are satisfactorily assayed by the proposed method are quoted, the results obtained being compared with those determined by the standard 18-hr., cup-plate method. J. A.

Organic

Chemical Microscopy of Essential Oils. IV. Cassia and Cinnamon Oils. L. W. Greene (*Amer. J. Pharm.*, 1947, **119**, 59–65)—Three kinds of cinnamon oil: (*a*) cassia, (*b*) cinnamon bark, and (*c*) cinnamon leaf oils, were examined with the following alkaline solutions—(I) a saturated solution of sodium hydroxide in absolute alcohol, (II) 30 per cent. sodium hydroxide solution, (III) sodium phenate solution (sodium hydroxide dissolved in phenol in equimolecular proportions and diluted with water to form a 20 per cent. solution), (IV) a saturated solution of potassium hydroxide in absolute alcohol, and with the following organic reagents—(V) phenyl hydrazine and (VI) benzidine.

Results—With (I), (*a*) gives a cloudy yellow amorphous precipitate, (*b*) gives crystals after 0·5 hr. at room temperature, and (*c*) gives long needle-like crystals. With (II) (one drop of reagent to one drop of oil on a slide), (*a*) and (*b*) give almost immediately a white or faint yellow crystalline mass, which develops a definite crystalline structure in 1 to 2 hr., and shows strong interference colours in polarised light. With (III), (*a*) and (*b*), in 10 min., form crystals of long slender microscopic needles which in polarised light show strong feathery markings in interference colours, and (*c*) forms no crystals in 1 hr. With (IV), (*a*) and (*b*) give crystals which are weakly anisotropic in polarised light and practically invisible in ordinary light, and (*c*) gives an anisotropic mass without definite crystalline structure. With (V) (one drop added to one drop of oil on a slide), (*a*) and (*b*) yield interlocking needles of crystalline phenylhydrazone, with form similar to that given by (V) with bitter almond oil, but the latter differs by exhibiting strong polarisation colours; (*c*) forms no crystals. With (V) (one drop added to one drop of oil on a slide), (*a*) and (*b*) form immediately a yellow anisotropic mass of crystals of perfect and imperfect diamond-shaped plates. To obtain with (VI) a reaction product suitable for microscopic examination, the amount of reagent used is just enough to wet the tip of a stirring rod. Photomicrographs of a number of the products are reproduced. E. B. D.

Colour Reactions of Some Unsymmetrical Diarylethylenes. D. S. Tarbell and E. G. Lindstrom (*J. Amer. Chem. Soc.*, 1946, **68**, 1930–1932)—It has been shown, mainly by Pfeiffer and Wizinger (*Ann.*, 1928, **461**, 132; *J. prakt. Chem.*, 1939, **154**, 1) that unsymmetrical diarylethylenes, containing electron-donating groups in the aromatic rings, form coloured addition compounds with a variety of substances. The usefulness of these compounds as detecting agents for a number of toxic substances has been studied with particular reference to arsenicals, such as lewisite or ethyldichloroarsine. The colours produced with these

last compounds were determined by adding a drop of the liquid arsenical to the solid ethylene. Dianisylpropylene, when mixed with about twenty times its weight of silica gel, gave a detectable pink colour with less than 1 μg. of lewisite when air containing a few micrograms of the arsenical per litre was drawn through the silica gel. The reaction, however, was inhibited by air of high humidity. The following table gives the colours produced by the action of various diarylethylenes and a liquid arsenical. Brief details for the preparation of the last five compounds are given in the original paper.

Compound	Colour produced
1 : 1-*bis*-(4-Methoxyphenyl)-ethylene	Dark red
1 : 1-*bis*-(4-Methoxyphenyl)-propylene	Dark red
1 : 1-*bis*-(4-Methoxyphenyl)-*iso*butene	No colour
1 : 1-*bis*-(4-Methoxyphenyl)-2-phenylethylene ..	No colour
1 : 1-*bis*-(4-Dimethylaminophenyl)-ethylene.. ..	Intense blue-green
1 : 1-*bis*-(4-Dimethylaminophenyl)-propylene ..	Intense blue-green
1 : 1-*bis*-(4-Dimethylaminophenyl)-*iso*butene ..	Green
1 : 1-*bis*-(3 : 4-Dimethoxyphenyl)-ethylene	Transient purple
1 : 1-*bis*-(4-Phenoxyphenyl)-ethylene	Orange red
1 : 1-*bis*-(4-Phenoxyphenyl)-propylene	Faint transient pink
1 : 1-*bis*-(4-Methylthiolphenyl)-ethylene	Transient light green
1 : 1-*bis*-(4-Methylthiolphenyl)-propylene	No colour

J. A.

Colorimetric Micro-method for the Determination of Formic Acid. W. M. Grant (*Anal. Chem.*, 1947, **19**, 206–207)—The gravimetric and titrimetric methods for the determination of formic acid, depending upon measurement of the amount of carbon dioxide or mercurous chloride formed in its reaction with mercuric chloride, are not applicable to the determination of amounts of formic acid less than 1 mg. To increase the sensitivity of the mercurous chloride method a colorimetric procedure has been developed, which permits the determination of amounts of 5 to 30 μg. in 1 ml. with an accuracy of ±1 μg. The method is based upon the chromogenic reduction of a mixture of phosphomolybdic and phosphotungstic acids by the washed mercurous chloride formed in the reaction. Formic acid itself does not give a colour with the reagent.

Procedure—To determine the relationship between the colorimetric readings and the formic acid concentration, prepare a series of dilutions of a standard sodium formate solution (44·4 mg. per litre) containing the equivalent of 0 to 30 μg. of formic acid per ml. To 1 ml. of each solution in a 15-ml., conical centrifuge tube add 0·5 ml. of a reagent containing 20 g. of mercuric chloride, 30 g. of sodium acetate, and 8 g. of sodium chloride in 100 ml. of water, and heat the mixture on the water-bath for 3 hr., preventing evaporation by protecting the upper two-thirds of the tube from excessive heating. After thorough cooling, add 2 ml. of a diatomaceous earth suspension (20 mg. of Dicalite laboratory Filter Aid in 100 ml. of water) to increase the bulk of the precipitate, and to prevent retention of the particles in the surface film add about 10 ml. of alcohol rapidly from a coarse burette tip. Centrifuge the tubes at 2000 r.p.m. for 10 min., after which the liquid can be decanted without loss of precipitate. Wash with two 10- or 15-ml. portions of water by centrifuging and decanting. To each washed precipitate add 1 ml. of the colour reagent. To prepare this dissolve 10 g. of phosphotungstic acid and 130 g. of phosphomolybdic acid in sufficient water at room temperature to yield 400 ml., then add 50 ml. of concentrated hydrochloric acid and 50 ml. of 85 per cent. phosphoric acid. Although a slight sediment forms, the supernatant light yellow solution is stable for several weeks in a stoppered Pyrex bottle. The gradual appearance of a green tinge is accompanied by a slight increase in the colour of the blank determination. Stir the precipitate by striking the tube with the finger and heat on the steam-bath for 15 min. Without cooling the tube, add 4 ml. of saturated sodium carbonate solution and measure the blue colour photo-electrically, plotting the galvanometer readings against the concentrations of formic acid. Residual diatomaceous earth does not interfere significantly with the colour measurement, there is no appreciable change in colour density in at least 10 min., and no turbidity appears when the mercurous chloride precipitate has been adequately washed.

Unknown samples to which the mercuric chloride method can be directly applied are treated in the same manner as the standard solutions and the formic acid concentration is determined by comparison of the colour density measurements with the standard values.

Formic acid in biological material (*e.g.*, blood) is first separated from interfering substances by protein precipitation and low-temperature distillation under reduced pressure in the presence of a strong acid. With blood, it was found satisfactory to centrifuge a mixture of 1 ml. of blood with 1 ml. of water and 1 ml. of 10 per cent. sulphosalicylic acid solution, then to add about 0·02 ml. of sulphuric

acid to the separated supernatant liquid and to distil this to dryness at room temperature. This distillation can be conveniently made in an appropriate evacuated and sealed tube (Grant, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 729) with the condenser cooled in a bath of dry ice. Recoveries of formic acid added to blood averaged 98 per cent. with an absolute deviation from the mean of 5·1 per cent.

At low concentrations of formic acid, there is a slight deviation from Beer's law, probably due to loss of some mercurous chloride in the washing water, and a slight scattering of the readings round the curve is probably due to mechanical losses. These combined errors amount to about ±1 μg. and are not diminished by reduction of the scale of the method, although slight improvement is obtained by the use of washing water saturated with mercurous chloride.

Samples to be analysed must be free from other reducing substances, such as formaldehyde and ascorbic acid. A. O. J.

Disintegration of Viscose (in the Analysis of Paper Fibres). B. L. Browning and J. H. Graff (*Paper Trade J.*, 1947, **124**, No. 9, Feb. 27, 134)—Papers treated with viscose are difficult to disintegrate by the usual procedures of fibre analysis, and the following method is recommended. Place the sample, torn into small pieces, in a beaker containing 50 per cent. calcium nitrate solution, and heat just below the b.p. When the paper starts to disintegrate, remove it, rinse it in hot water, and disintegrate it further by boiling it in 0·5 per cent. sodium hydroxide solution. Wash it successively with distilled water, cold 0·2 per cent. hydrochloric acid solution, and water again, and defibre the paper finally by rolling it into pellets and shaking these with water in a conical flask. The usual staining methods are unaffected by this procedure. The method is unsuitable for paper that has been treated with synthetic resins to produce wet strength. J. G.

Identification of Melamine. E. J. Candlin (*J. Soc. Dyers and Colourists*, 1947, **63**, 144)—Published methods having proved unsatisfactory, the formation of a picrate was investigated. A yellow precipitate is obtained on mixing a neutral melamine solution with concentrated, aqueous picric acid solution; it melts at 312° to 315° C. (uncorr.) after recrystallisation from water. Since formaldehyde inhibits its formation, a method of simultaneous hydrolysis and oxidation is used when melamine - formaldehyde compounds are being examined.

Procedure—Add 5 g. of melamine - formaldehyde condensate to 250 ml. of dilute sulphuric acid and heat to 70° C. Add solid sodium permanganate to decolorise the solution, and filter off carbonaceous matter and manganese oxides. Decolorise the solution with sulphur dioxide, add an excess of sodium hydroxide to precipitate dissolved manganese, and boil. Filter again, neutralise the filtrate with sulphuric acid, and add an excess of saturated, aqueous picric acid. The derivative forms rapidly.

As potassium and ammonium ions form explosive picrates, they must be excluded from the solution. The following oxidising mixtures were unsuitable; sodium hydroxide and hydrogen peroxide, sodium chromate in acid solution, sodium persulphate in hydrochloric acid, and manganese dioxide in hydrochloric acid.

Satisfactory qualitative results have been obtained on melamine - formaldehyde condensates and on fabrics treated with this type of product, but, as much of the resin originally present may disappear during hydrolysis and oxidation, only positive tests may be safely regarded as conclusive. M. E. D.

Inorganic

Ferrous Ethylenediamine Sulphate as an Oxidimetric Standard. K. P. Caraway and R. E. Oesper (*J. Chem. Educ.*, 1947, **24**, 235–236)—Ferrous ethylenediamine sulphate $(CH_2NH_2)_2SO_4.FeSO_4.4H_2O$, is easily prepared, purified, and dried, and has been shown to be unoxidised after 149 days' standing in air; it is neither deliquescent nor efflorescent.

Preparation—Add 60 ml. of 6 *N* sulphuric acid to 10 g. of 98 per cent. ethylenediamine solution. Add 46·3 g. of ferrous sulphate and, when dissolution is complete, dilute to 300 ml. with water. Stir with 300 ml. of ethanol and filter on a Buchner funnel, washing with 50 per cent. ethanol. Dissolve the precipitate in acidified water, and add two-thirds of the volume of alcohol to reprecipitate the salt. Filter again, and wash with 65 per cent., and finally 95 per cent., ethanol; dry at 50° C. (*cf.* Grossman and Schuck, *Z. anorg. Chem.*, 1906, **50**, 26).

Use as a standard—To standardise a 0·05 *N* oxidising solution, dissolve 0·4 g. of ferrous ethylenediamine sulphate in 150 ml. of water and 10 ml. of diluted sulphuric acid (1 + 1). When using dichromate, add also 5 ml. of diluted phosphoric acid (1 + 1). Titrate then with the oxidising solution using an appropriate indicator.

The salt has been used to standardise ceric sulphate, potassium permanganate, and potassium dichromate solutions and, in the range of 0·02 to 0·2 *N* solution, the results agree well with those given by the usual methods.

Ceric sulphate solution has been standardised against (i) ferrous ethylenediamine sulphate, (ii) sodium oxalate, and (iii) potassium dichromate through sodium thiosulphate, and the 9 values given were all either 0·0499 or 0·0500 *N*. M. E. D.

Use of Cacotheline in Volumetric Analysis. I. Determination of Calcium Salts by Titration with Sodium Oxalate. II. Determination of Tervalent Iron by Titration with Stannous Chloride Solution. M. L. Kutschment and A. I. Gengrinovitsch (*Zavod. Lab.*, 1945, **11**, 267–269)—*Determination of calcium*—Hitherto no direct method of titrating calcium has been described. It is now shown that cacotheline may be used as an indicator in presence of ferrous sulphate with sodium oxalate as titrating solution. When all the calcium has been precipitated, sodium oxalate starts to combine with tervalent iron and favours the reduction of cacotheline by the ferrous salt. The end-point is the appearance of a violet colour.

Procedure—To the solution of the calcium salt, neutral or acid with acetic acid, add 1 ml. of a saturated aqueous solution of cacotheline, and one drop of a saturated solution of ferrous sulphate, and titrate with 0·1 *N* sodium oxalate until a violet colour appears. The reaction is rapid and the titration takes only 1 to 2 min. The colour is stable for several minutes. In acetic acid solution, magnesium salts may be present to at least five times the quantity of calcium. Results are accurate to about 1 part in 300.

Determination of iron—Cacotheline, present in a ferric solution which is titrated with stannous chloride solution, is not reduced until all the iron is in the ferrous state.

Procedure—To the solution of ferric iron in 2 *N* hydrochloric acid add 1 ml. of cacotheline solution, heat to boiling, and titrate with standardised stannous chloride solution to the appearance of a violet colour. Prepare the stannous chloride solution by dissolving 30 g. of stannous chloride in a mixture of 300 ml. of concentrated hydrochloric acid and 700 ml. of water by boiling, and establish the titre on potassium iodate in presence of starch (*cf.* Korenman, "*Quantitative Microchemical Analysis*," 1936, p. 143). The end-point is very sharp. Results are accurate to 2 or 3 parts in 1000. G. S. S.

Determination of Traces of Copper by Extractive Dithizone Titration. C. H. Schonk (*Chem. Weekblad*, 1946, **42**, 295–301)—The speed of reaction of copper with dithizone solution depends on the *p*H value, increasing with an increase in the *p*H. A quick reaction is desirable, as it makes the titration sharper. On the other hand, increasing the *p*H results in interference by zinc, so that a *p*H of 2·8 represents an optimum value for this determination in simple aqueous solution. In presence of large concentrations of salts, the speed of reaction decreases above *p*H 2·8, but the interference by zinc is also less, so that for such solutions a *p*H of 3·3 is chosen. The indicator used for adjustment of the solutions is the potassium salt of benzenesulphonic acid azo-benzylaniline. The reaction is also accelerated by various impurities, and for this reason the dithizone is not subjected to a purification process. Chromium also accelerates the reaction. Since the reaction is an equilibrium one, the titration is not directly proportional to the copper present, as shown by the following table:

μg. Cu	ml. dithizone
1	1·0
2	1·8
4	3·4

Thus, the titre of the solution must be determined against a standard copper solution of a similar concentration and composition to that of the unknown. The amount of zinc present should not exceed 500 μg. per 100 ml. for water solutions and 100 μg. for solutions prepared by wet destruction. Interference by mercuric and silver ions may be prevented by addition of 0·3 ml. of a 50 per cent. solution of potassium iodide. Bismuth reacts after copper, and does not interfere if standardisation is carried out on the titrated solution. Stannous salts are oxidised by hydrogen peroxide, the latter being removed by sulphite. Ferric iron should not exceed 60 μg. for water solutions, or 2000 μg. for solutions prepared by wet oxidation. Larger quantities may be masked by sodium fluoride, of which 10 mg. are sufficient for 1·5 mg. of iron. If organic matter is destroyed by wet oxidation with sulphuric and nitric acids, it is important to remove all nitric acid.

Special reagents, other than copper-free water, acids, etc., are as follows—*Dithizone solution:* a solution of the commercial compound in carbon tetrachloride containing about 2 mg. per 100 ml. About 3 ml. should be used in the titration. This solution is kept in a separating funnel under a layer of a solution of sodium sulphite in 2 *N* sulphuric acid. *Chromium solution:* a 20 per cent. solution of $Cr_2(SO_4)_3,18H_2O$ with a few drops of sulphuric acid, freed from copper by extraction with dithizone, and then washed with carbon tetrachloride.

Procedure—To 100 ml. of the solution, in a separating funnel, add any masking reagents, and a few drops of indicator, and adjust the *p*H to 2·8 or 3·3 (see above). Add three drops of chromium solution (this is unnecessary after wet combustion), and add the dithizone solution from a microburette, at first in 0·4-ml. portions, and finally in 0·1-ml. portions. After each addition shake vigorously for 45 sec., and allow to settle. Before each successive portion is added the preceding portion is run off. Continue the titration until the tetrachloride layer has a distinct green colour. At this point there is an excess of dithizone, and to correct for this only the half of the last portion added is reckoned in the measurement. If the amount of copper is very small, the liquid should

first be saturated with carbon tetrachloride. After the completion of the titration, wash the liquid with a small amount of the tetrachloride, add a quantity of standard copper solution approximately equal to that found, and carry out another titration in order to standardise the dithizone solution under the same conditions as those of the original titration. G. M.

Determination of Available Chlorine [in Paper]. W. H. Birchard (*Pulp and Paper Mag. Canada*, 1947, **48**, Feb., 62)—Existing methods (*e.g.*, *T.A.P.P.I.* Standard T.611 m–45) in which the difference between the total chlorides, determined by oxidation with hydrogen peroxide and titration with standard silver nitrate, and the available chlorine, determined by titration, with standard sodium thiosulphate, of the iodine liberated from potassium iodide solution in presence of acetic acid, is taken to give the chlorides present, actually only indicate the amount of chloride present in excess of the chloride formed (as calcium chloride) when calcium hypochlorite is formed by passing chlorine into lime water. A similar error exists with the arsenious acid method. They arise from the convention of expressing the results in terms of bleaching powder containing 35 per cent. of chlorine. The methods should be revised so as to give the result in terms of chlorine available for bleaching, *i.e.*, of the hypochlorite content. J. G.

Analysis of Mixtures of Mercurous and Mercuric Mercury and Sulphuric Acid. B. Warshowsky and P. J. Elving (*Anal. Chem.*, 1947, **19**, 112–114)—In order to find the efficiency of a used mercuric sulphate catalyst solution, the total mercury is determined by titration with standard thiocyanate after oxidising the reduced mercury present with ceric sulphate. Mercurous salts are determined separately by oxidation to the mercuric iodide complex with iodine liberated from an excess of standard iodate solution, and determination of the excess of iodine. The mercuric content is determined by difference. The sulphuric acid is titrated with standard alkali in presence of an excess of sodium chloride to prevent buffering by hydroxy-mercuric compounds, and to precipitate mercurous chloride.

Procedure—Total mercury—Treat a sample of the catalyst solution containing 0·1 g. of mercury salts with 100 ml. of water, 20 ml. of diluted sulphuric acid (1 + 1), and 50 ml. of 0·1 *N* ceric sulphate containing 30 ml. of concentrated sulphuric acid per litre. Oxidise the mercury by boiling for 20 to 30 min., cool, and add 3 drops of *o*-phenanthroline ferrous indicator. From a burette add 0·2 *N* ferrous sulphate solution (39 g. of ferrous ammonium sulphate crystals diluted to 500 ml. with 0·1 *N* sulphuric acid) almost to the equivalence point to remove the excess of ceric ions, but leaving the solution coloured slightly green. Add 2 ml. of 40 per cent. ferric sulphate solution and titrate with 0·1 *N* potassium thiocyanate between 15° and 20° C. A blank correction is unnecessary, and any precipitate of mercuric thiocyanate formed near the end-point can be disregarded.

Mercurous mercury—Treat a sample containing approximately 0·25 g. of mercurous mercury with 25 ml. of 0·1 *N* potassium iodate, 1 g. of potassium iodide dissolved in a few millilitres of water, and 10 ml. of *N* sulphuric acid, and stopper immediately. Shake to dissolve the precipitate first formed, and then rinse the stopper and titrate the washings and solution with 0·1 *N* thiosulphate, in presence of starch.

Sulphuric acid—Add 10 ml. of 10 per cent. sodium chloride solution to a sample containing 0·25 g. of sulphuric acid and dilute to 150 ml. Titrate with 0·1 *N* sodium hydroxide in presence of methyl red. M. E. D.

Determination of Aluminium in High Alloy Steel. E. I. Fogelson and N. V. Kalmikova (*Zavod. Lab.*, 1945, **11**, 359–360)—After removal of silicon, and electrolysis with a mercury cathode, manganese is precipitated by means of persulphate, and titanium, vanadium, and iron in solution are thrown down by means of cupferron. Adjustment of the *p*H then gives a precipitate of aluminium as its cupferron complex, free from other metals. The method is claimed to be quicker than the usual methods, such as the 8-hydroxyquinoline method, and to give an uncontaminated precipitate.

Procedure—Dissolve 0·5 g. of sample by heating with 40 ml. of diluted sulphuric acid (1 + 3), oxidise with nitric acid, evaporate to fuming, dissolve the residue in water, and filter. Ignite the insoluble silica, volatilise it with hydrofluoric acid, fuse the residue with potassium pyrosulphate, dissolve the melt in water and return it to the main solution. Electrolyse the solution as usual, using a mercury cathode, then heat the electrolyte, preferably after evaporation to a volume of 100 ml., with 2 g. of ammonium persulphate until manganese is completely precipitated, and filter. Add to the filtrate 8 ml. of concentrated sulphuric acid, dilute with water to 200 ml., and add 2 per cent. cupferron solution to precipitate titanium, vanadium, and iron. Filter and neutralise the filtrate carefully, after making it very cold and stirring, with ammonia in presence of Congo red indicator, and add 20 ml. of buffer mixture to give a *p*H of 4 to 5. The buffer mixture is prepared by neutralising 6 ml. of glacial acetic acid with aqueous ammonia to litmus, adding 3 ml. of glacial acetic acid, and diluting with water to 100 ml. Normally the excess of cupferron remaining in the solution after precipitation of titanium, etc., is sufficient for the precipitation of aluminium, but with large amounts

of aluminium, add a further 3 to 5 ml. of cupferron solution. Filter and ignite preferably as described by Zvenigorodskaja and Tschernikov (*Zavod. Lab.*, 1940, **9**, 1089). G. S. S.

Colorimetric Determination of Iron in Brass and Bronze. W. Goodman (*Anal. Chem.*, 1947, **19**, 141–142)—Hitherto the failure of colorimetric methods for this determination has been due to loss of iron by co-precipitation in separating the other constituents. This is avoided by direct determination in solution.

Procedure—Treat a 1-g. sample in a 200-ml. iron-free beaker (Vicor) with 15 ml. of water, 0·5 to 1·0 ml. of 48 per cent. hydrofluoric acid, and 10 ml. of nitric acid (sp.gr. 1·42). Cover with a platinum lid, set aside until dissolution is complete, and then boil to expel oxides of nitrogen. Rinse the lid with water, and dilute the solution and washings to 135 ml. Add 1 drop of 0·1 *N* hydrochloric acid, and deposit lead and copper by electrolysis at a current of 2 amperes. Reserve the electrolyte for the iron determination.

Dilute the solution accurately to 150 ml. and pipette 1 ml. into a colorimetric tube. Add 18 ml. of hydroxylamine hydrochloride solution (4 g. of the salt, 50 g. of ammonium acetate and 35 ml. of concentrated hydrochloric acid to 1 litre, adjusted to *p*H 4·3 with the acetate or acid. Add 6 ml. of 0·15 per cent. *o*-phenanthroline solution, stopper, and shake thoroughly. Determine the percentage transmittancy of the orange coloration by means of a Fisher electrophotometer, using a No. 425 dark blue filter, adjusted to 100 per cent. transmittancy with distilled water treated as above. Determine the iron content by reference to a calibration curve of percentage transmittancy plotted against iron concentration on semi-logarithmic paper. This curve serves also as a blank determination for the reagents and vessels used.

Results—Using National Bureau of Standards samples ranging from 0·03 to 0·83 per cent. of iron, the average results obtained agreed closely with the certified values.

The presence of fluoride ion does not interfere at *p*H 4·1. Interference due to zinc is avoided by using an excess of *o*-phenanthroline. Aluminium and manganese in amounts up to 250 times the iron concentration, and nickel up to 1 per cent., do not interfere with the method. Iron added to samples containing 4·8 and 9·7 per cent. of tin was quantitatively recovered. M. E. D

Analysis of Cassiterite. T. L. Pokrovskaja (*Zavod. Lab.*, 1945, **11**, 363–364)—The determination of silica, titania, niobium and tantalum pentoxides, ferric oxide, zirconia, calcium, magnesium, manganese, tungsten, arsenic, heavy metals, and tin is outlined and improved procedures are detailed.

Procedure—The sample (2 to 5 g.) of cassiterite is reduced in hydrogen and tin is volatilised as stannic chloride (this is normal Russian practice). Heat the dry residue with concentrated hydrochloric acid and a few drops of bromine water, evaporate to dryness to remove bromine, and again treat with concentrated hydrochloric acid. Dilute with water, leave the solution just acid after adding aqueous ammonia, add 3 g. of ammonium chloride for each 100 ml. of solution, and heat to boiling. To precipitate niobium, tantalum, titanium, zirconium, and residual tin, add 20 per cent. aqueous pyridine solution until a definite odour of pyridine persists, and then add an excess of 15 to 20 ml. Heat to boiling and allow the solution to stand on a water-bath for 30 to 40 min. to coagulate the precipitate. The solution contains only calcium, magnesium, and manganese, which are determined by normal methods. The advantage of the pyridine precipitation over the normal method is that the earth acids, tin, titanium, zirconium, iron, etc., are all precipitated together and are not distributed between a precipitate and a solution. Filter off the precipitate, wash with 3 per cent. ammonium chloride solution, containing a few drops of pyridine, ignite in a quartz crucible and fuse with potassium pyrosulphate. Dissolve the melt in 20 per cent. tartaric acid solution, filter off the silica (ignite, weigh, treat with hydrofluoric acid, etc., as usual), and pass hydrogen sulphide through the filtrate to precipitate residual tin and other heavy metals. Filter and reject the insoluble material (heavy metals are best determined on a separate sample). Add ammonia to precipitate ferrous sulphide, and then filter again. Determine iron by dissolving the sulphide in 15 ml. of concentrated hydrochloric acid, with a few drops of nitric acid added after solution, and weighing as Fe_2O_3 or determining colorimetrically with sulphosalicylic acid (Nikitina, *Zavod. Lab.*, 1940, **9**, 629). Add to the filtrate from the ferrous sulphide sufficient hydrochloric or sulphuric acid to give a 10 per cent. acid content, boil off hydrogen sulphide, and then add 6 per cent. cupferron solution to precipitate the earth acids, titanium, and zirconium. Filter and wash the insoluble matter with 1 per cent. hydrochloric or sulphuric acid solution, containing cupferron. Carefully dry the precipitate, ignite, and weigh; then fuse with pyrosulphate and treat the melt with 1 per cent. tannin in 10 per cent. hydrochloric acid. Boil the solution, filter, ignite, and weigh the earth acids, make the filtrate 10 per cent. in hydrochloric acid, cool, and precipitate zirconium and titanium by means of 6 per cent. cupferron solution. Filter off the precipitate, ignite, weigh, fuse with pyrosulphate, and determine titanium colorimetrically with hydrogen peroxide, and zirconium as phosphate.

On a separate portion determine tungsten, arsenic, and tin by first fusing with sodium peroxide. Acidify the alkaline solution with hydrochloric acid, making the acid content 50 per cent., and precipitate arsenic by means of sodium hypophosphite. Filter and determine arsenic iodimetrically. Determine tungsten colorimetrically with stannous chloride, and tin by the normal iodimetric method.

On a further separate portion carry out the reduction and the removal of tin as in the main method, treat the residue with concentrated hydrochloric acid, filter off the insoluble matter, and precipitate heavy metals from the filtrate by means of hydrogen sulphide, and determine them by the usual methods. G. S. S.

Gas Analysis

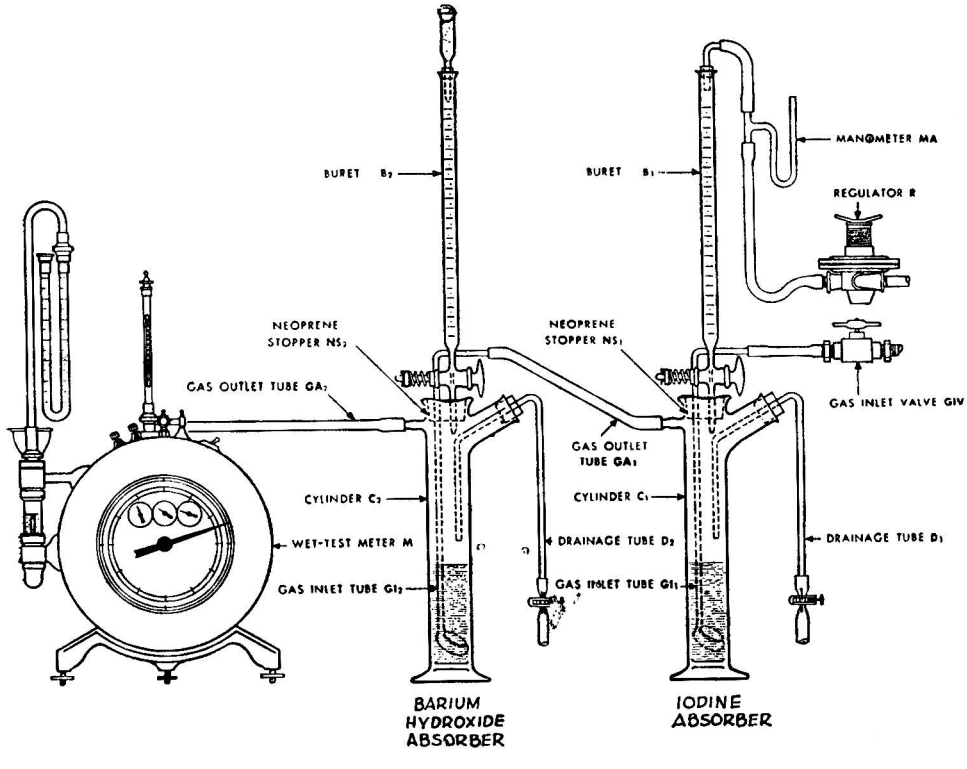
Simultaneous Determination of Hydrogen Sulphide and Carbon Dioxide in a Continuous Gas Stream. C. L. Blohm and F. C. Riesenfeld (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 373–376)—The method is based on the reactions

$$H_2S + I_2 \rightarrow 2HI + S$$

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

The apparatus is shown in the figure. The absorption vessels are 500-ml. Pyrex hydrometer jars, modified by addition of side arms. All the stoppers and flexible tubing in contact with the gas are of neoprene, as rubber absorbs some hydrogen sulphide. The gas inlet tubes are fitted with sintered-glass dispersion discs. These should be of coarse porosity to avoid blocking of the pores by the precipitated sulphur and barium carbonate. The iodine solution in burette B_1 is kept under a pressure of air or neutral gas of about 150 to 250 mm. of mercury to overcome the pressure in the apparatus.

Method—Put in vessel C_1 150 ml. of water free from carbon dioxide, 5 ml. of 0·4 per cent. starch solution, and enough 0·1 *N* iodine to give a slight but permanent blue colour. Put in vessel C_2 150 ml. of carbon-dioxide-free water and 5 ml. of 0·1 per cent. phenolphthalein solution. Add from the burette B_1 a known volume of 0·1 *N* iodine and from burette B_2 a known volume of 0·25 *N* barium hydroxide. Pass the gas through the apparatus at a rate of 1 to 2 cubic feet per hour, and record the gas meter readings at which the indicators change colour. Add further titration fluids and repeat the procedure. In special cases, use titrating fluids of other concentrations. Iodine from 0·01 *N* to 0·5 *N* and barium hydroxide from 0·1 *N* to 0·5 *N* are suitable. The first readings of a series are discarded as some of the gas is used to saturate the absorbing liquids. Correct the volume of the gas as indicated on the meter for temperature, barometric pressure, water vapour pressure, the volume of the absorbed gases, and the



volume of gas displaced by the addition of titrating fluids.

1 ml. of 0·1 *N* iodine ≡ 1·183 ml. of hydrogen sulphide at 60° F. and 30 in. of mercury.

1 ml. of 0·1 *N* barium hydroxide ≡ 1·183 ml. of carbon dioxide at 60° F. and 30 in. of mercury.

Tests of the method on natural gas indicate that the variations between successive determinations do not exceed 2·5 per cent. The method does not discriminate between hydrogen sulphide and mercaptans or other reducing gases, or between carbon dioxide and other acidic gases. L. A. D.

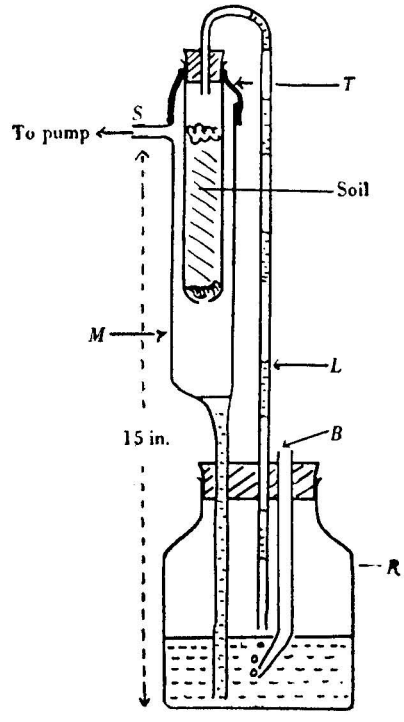
Water Analysis

Determination of Dissolved Oxygen in Presence of Sulphite. C. Janssen (*Chem. Weekblad*, 1946, **42**, 115–119)—In the original Winkler method for the determination of dissolved oxygen in water, the presence of sulphite interferes for two reasons. Iodine reacts with the sulphite in acid solution, and oxygen is used up, not as previously supposed by direct oxidation of the sulphite by the manganous acid formed, but by the catalytic action of the manganese on the reaction between oxygen and sulphite. By the modified manganese carbonate method (Winkler, *Z. anal. Chem.*, 1905, **53**, 665; Bruhns, *Chem. Ztg.*, 1915, **39**, 845; 1916, **40**, 45, 71, 985, 1011; Goldina, *Ber. allruss. warmetechn. Inst. No.* 6, 1934, 43; *Chem. Zentr.*, 1935, II, 2102) low values are also obtained. The method of Haase (*Z. anal. Chem.*, 1937, **90**, 241) employs iodine to remove the sulphite and thiosulphate to remove excess of iodine, but results are also low owing to rapid oxidation of the tetrathionate. Correct results may be obtained by the original method of Winkler if a correction is applied for the sulphite present. Two bottles are filled with the water. In one, determine the oxygen content according to the ordinary Winkler method. In the other, determine the sulphite content by a direct titration of the water with iodine and not by adding an excess of iodine and titrating back. G. M.

Physical Methods, Apparatus, etc.

Operating Characteristics of the Sargent Model XX Visible Recording Polarograph. J. J. Lingane (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 734–738)—The performance of this American instrument is compared with that of other American recording polarographs, and most of the criteria mentioned can be applied to British instruments. The instrument should be robust and immune to vibrations, and adequate electrode assembly and cells should be provided. A continuously variable sensitivity control and a visible recording system are advantageous, and it should be possible to record diffusion currents as a function of time at constant applied e.m.f. The observed diffusion currents and half-wave potentials must be independent of the degree of damping used, and the current sensitivity must be constant. J. G. W.

Simple Automatic Percolator. H. Lees (*J. Agric. Sci.*, 1947, **37**, 27–28)—The apparatus enables automatic percolation of an aerated solution, and changes due to passage through the column



may be determined by analyses of the solution returned to the reservoir. It is suitable for soils, bacteria or fungi cultures on porous media, extractions from solids, and some types of chromatography; the gas used may also be varied by using a closed-system pump.

Place 10 to 20 g. of the solid material between plugs of glasswool in a 6 × ¾ in. Pyrex test tube, with a hole in the bottom. *T* is a piece of 1¼-in. bicycle inner tube. The outer tube, *M*, is a 8 × 1¼-in. Pyrex tube, fused to a piece of 5-mm. internal diameter Pyrex tubing, and 15 in. above its join is a side-arm, *S*. Through the bung of the reservoir, *R*, passes a bubbler, *B*, and above its submerged end the lift tube, *L*, which is held in the end of the soil tube by a bung. Apply slight suction at *S* and bubbles of air and liquid pass up *L*; the air is drawn off at *S* and the liquid is returned into *M*. Isolate the system from the pump, and pipette samples from the reservoir for analysis. Waterlogging is impossible as the decrease of pressure in *M* lowers the liquid level in *R* below

the end of *L* and percolation stops. The depth of the end of *L* below the liquid surface does not affect percolation, though it affects the head of liquid in *M*. M. E. D.

Precise Low-Pressure Measurements with a Thermocouple Gauge. W. G. Smiley (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 800–801)—Pressure gauges that depend on thermal conductivity (Pirani and thermocouple gauges) are usually operated either at constant current or at constant voltage, when the upper limit of the sensitivity range is due to the temperature coefficient becoming too small for measurement. By operating at constant temperature (constant resistance on the Pirani gauge, constant output on the thermocouple gauge), the range may be considerably extended and precise measurements may be made.

The heater current of a General Electric Type J–1 vacuum gauge was adjusted to give a constant thermal e.m.f. of 3·050 millivolts. The necessary heater current, which is a measure of the pressure, was determined to ± 0·01 milliamp. by measuring the voltage drop across a 0·1 ohm precision resistor. The current varied from 27 milliamp. (below 0·001 mm.) to 150 milliamp. (above 20 mm.). In any one run the gauge was sensitive to a 1 per cent. change in pressure from 0·002 to 20 mm., or to a 0·1 per cent. (or less) change from 0·02 to 2 mm. Since readings were found to vary between runs, the gauge was enclosed in a constant-temperature water-jacket.

The curved characteristic of a thermal pressure gauge necessitates extensive calibration. For measuring the pressure of water vapour above hydrates, the vapour pressure of ice, which is known to within ± 0·2 per cent., is suggested as a convenient standard. J. T. S.

Vacuum Micromanometer. W. S. Young and R. C. Taylor (*Anal. Chem.*, 1947, **19**, 133–135)—Details are given of the construction and calibration of a manometer suitable for measuring pressure in the range 10^{-1} to 10^{-3} mm. of mercury. The pressure is measured by observing the position of a bubble of gas in a capillary tube connecting two large reservoirs of pentane. Pressure changes are transmitted to the pentane by two barometric legs of mercury. The head of one mercury column is in a high vacuum and the gas, the pressure of which is to be measured, is placed in contact with the head of the other mercury column. Differences between pressure measurements made on the same samples of air with the micromanometer and with a McLeod gauge, in the pressure range 10^{-2} to 10^{-1} mm. were not more than $\pm 4 \times 10^{-3}$ mm. and averaged less than $\pm 10^{-3}$ mm. The use of the manometer for molecular weight determinations is described in another paper (*see the next abstract*). B. A.

Molecular Weight Determination with a Vacuum Micromanometer. W. S. Young and R. C. Taylor (*Anal. Chem.*, 1947, **19**, 135–137)—To determine the molecular weight of a liquid, small quantities are allowed to vaporise at room temperature into a large bulb, previously evacuated, and the resultant pressures are measured by a micromanometer of the type described in the previous paper (*Idem., Ibid.*, p. 133; see preceding abstract). The liquid is introduced into the evacuated bulb through a mercury-sealed, sintered-glass disc, F porosity, which is porous to most liquids, but not to mercury. A micro-burette suitable for measuring the liquid sample is prepared from thermometer tubing selected to deliver about 2×10^{-4} ml. per cm. and having 20 to 30 graduations per cm. length. One end is ground to a truncated cone to ensure good contact between the capillary and the sintered disc.

The molecular weights of many organic liquids can be determined with an average accuracy of about ± 2 per cent. Liquids to which the method cannot be applied are those that react with mercury, or have vapour pressures below 0·1 mm. of mercury at room temperature. B. A.

Apparatus for Determining Boiling Points. L. M. Simmons (*J. Chem. Educ.*, 1947, **24**, 233–234)—The apparatus is a glass U-tube of 7-mm. bore with limbs 15 cm. and 9 cm. long. The shorter limb can be closed by a ground plug and the joint sealed by mercury in a mercury cup. Both limbs are graduated in millimetres from a datum line near the bend.

Procedure—Add mercury to reach half way up the scale on the shorter limb, exert pressure to push the mercury to within 2 mm. of the ground socket, and pour about 0·3 ml. of the sample on to the mercury surface beneath the socket. Remove any air bubbles, insert the stopper, and release the pressure. From the barometric pressure and the levels of the mercury in the two limbs calculate the position of the mercury level in the longer limb at which the pressure of the vapour would be 760 mm. Place the tube vertically in a bath of a suitable liquid, heat the bath slowly with stirring, and note the temperature at which the mercury is at the calculated level. Take a further reading as the temperature falls and repeat until good concordance is obtained.

As the volume occupied by the vapour is small and there is no distillation of the sample, the method may be applied to liquid mixtures and may be used to test for the presence of dissolved air and other impurities in a liquid. The reproducibility of results is ± 0·1° C. B. A.

Errors in Spectrochemical (Flame) Analysis. A. C. Oertel and H. C. T. Stace (*J. Soc. Chem. Ind.*, 1946, **65**, 350–354)—A statistical analysis has

been made of the errors in determinations of the exchangeable cations in soils by means of an air-acetylene flame and a large quartz spectrograph. Even with an elementary technique an average standard error of less than 4 per cent. was obtained. Most of the error was due to variations in the photographic plates, and the significance of this in relation to the placing of the standard spectrograms on the plate is discussed. In general, a large quartz spectrograph is not suitable for use with an air-acetylene flame because the very low light-collecting power of the instrument necessitates very long exposures or the use of extremely concentrated solutions. B. A.

Reviews

THE PHARMACOPOEIA OF THE UNITED STATES OF AMERICA. Thirteenth Revision (U.S.P. XIII). Pp. cvii + 957. Mack Publishing Co., Easton Pa. Price 8 dollars.

While, to the exasperation of its Editor, the revised post-war edition of the British Pharmacopoeia, owing to printing difficulties, is still in the press, the results of the thirteenth revision of the United States Pharmacopoeia have become available. The U.S.P. XIII came into force on April 1st, 1947, five years after the publication of the twelfth revision, and its contents reflect a period of intensive medical development that has been the outcome of the scientific research stimulated by the second world war. The trend of medical opinion in the United States is indicated by the appearance of ninety-five new monographs and the deletion of monographs on one hundred and twelve substances that appeared in the U.S.P. XII. Monographs deleted include those for lactic, mandelic, phosphoric and sulphuric acids, chloroform water, silver proteinate, belladonna root, bismuth subnitrate, carbon tetrachloride, chloramine-T, decoctions, infusions and several extracts (including extract of malt), reduced iron, nux vomica, ergot, colchicum seed, strophanthin, Blaud's pill, several oils and spirits, antimeningococcus and antipneumococcus sera, salol, prepared suet, sulphapyridine and terpin hydrate. The deletions are indeed striking but scarcely more so than the admissions. Among monographs appearing in the U.S.P. for the first time are those for aluminium phosphate gel, anhydrohydroxyprogesterone (for which Ethisterone is the British approved name), antimony sodium thioglycollate, bentonite magma, benzalkonium chloride (a mixture of alkyldimethylbenzyl ammonium chlorides used in aqueous solution as a detergent), carbachol (carbamylcholine chloride), cholera vaccine, desoxycorticosterone acetate, digitoxin, digoxin, diphtheria and tetanus toxoids, helium, methyl testosterone, penicillin salts and preparations, plague vaccine, progesterone, methyl and propyl hydroxybenzoates (under the names of methylparaben and propylparaben respectively), sodium ascorbate injection, sulphamerazine (2-sulphanilamido-4-methyl pyrimidine), testosterone proprionate, soluble thiopentone, vinyl ether and epidemic typhus and yellow fever vaccines. Many of these substances have become well established in British medicine and monographs for such have already appeared in the Addenda of the British Pharmacopoeia and Supplements of the British Pharmaceutical Codex that have been issued during the war years.

It is not only the trend in modern medicine from the use of vegetable drugs and galenicals to the use of isolated standardised constituents and synthetic drugs that is particularly of interest to analysts, but also the trend towards demanding and achieving more specific standards for substances whether of chemical or biological origin. Reference Standards additional to the International Standards set up by the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations are available from the U.S.P. authorities to enhance the accuracy of many chemical, biological and microbiological assays.

It is of particular interest to note that U.S.P. Reference Standards are provided and required (*a*) for the determination of diethylstilboestrol (stilboestrol) in capsules, tablets and injections; (*b*) for the determination of epinephrine (adrenaline) in solutions such as the injection, inhalation and liquor; (*c*) for the determination of the mixed melting-point of methyltestosterone isolated in the assay of tablets. For sulfanilamide (sulphanilamide) a Reference Standard is provided, although it is not required for carrying out the examinations and assays described in the monographs for this substance or for the tablets.

An assay for each vitamin present is described in monographs on Hexavitamin capsules and tablets, which are each required to contain vitamin A, 5000 U.S.P. units; vitamin D, 400 U.S.P. units; ascorbic acid, 75 mg.; thiamine (aneurine) hydrochloride, 2 mg.; riboflavine, 3 mg.; nicotinamide, 20 mg. Vitamins A and D are determined biologically, riboflavine and nicotinamide microbiologically, aneurine by the thiochrome method and ascorbic acid by

the use of dichlorophenolindophenol, the precise methods being described in a section dealing with general tests, processes and apparatus occupying 260 pages.

The monographs on penicillin salts and preparations are circumscribed by the requirements of the Federal Food and Drug Administration. The calcium and sodium salts must comply with F.D.A. requirements. It is in striking contrast with the high potencies that are now issued by British manufacturers that for oral administration a minimum potency of 300 units per mg. is permitted; for aqueous injection, a minimum potency of 500 units per mg. except for material containing not less than 90 per cent. of penicillin X (penicillin III) when a potency of not less than 350 units per mg. is permitted; for suspensions containing 100,000 to 200,000 units per ml., calcium salt of minimum potency of 750 units per mg. may be used, though for those containing 300,000 units per ml. the minimum potency must be 900 units per mg. Material now issued from British manufacture, for all purposes, is not lower than the highest of the minimum potencies there described. All ingredients of the formulae used for penicillin dental cones, ointments, tablets and lozenges must be approved by the Federal Food and Drug Administration. All who are interested in the analysis of medicinal substances and preparations will find much of interest in noting the standards, tests and assays adopted by the U.S.P. The layout of the monographs facilitates reference, and it is a new departure that the titles are in English with sub-titles in Latin. Structural formulae are set out graphically although not always with typographical elegance. The paper and binding are excellent, in contrast with those available in present-day Britain, but it was surprising to discover that in the review copy pages 725 to 756 inclusive were missing. FRANK HARTLEY

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Fourth Edition. Vol. VIII. METH - OILS, ESSENTIAL. Pp. 679. London: Longmans Green & Co., Ltd. 1947. Price 80s.

The Editorial Board now responsible for the production of "Thorpe" (*cf.* ANALYST, **1946, 71**, 395) develops in this eighth volume the policy announced in the seventh volume—and they do it well. Of course there are difficulties inevitable in such a production under present-day restrictions, and others due to the time which must elapse before the whole series can be completed. For example: indexing. There was an index to the first six volumes at the end of Vol. VI, and now each volume is separately indexed; this is necessary and most useful, even if inconsistent. On the other hand, an inconsistency that should be eliminated is in methods of giving references: in some articles they are inset as heretofore; in others there is just a number corresponding to a bibliography at the end. These are, however, minor matters. We can, and do, very much welcome some of the new major articles in this volume on very modern topics, *e.g.*, on mineral and X-ray analysis by Dr. F. A. Bannister, on molecular infra-red spectra by Dr. Sutherland and visible and ultra-violet spectra by Dr. Morton, on nomenclature and on chemical literature. With regard to these latter articles it is noted that Dyson's new proposals are not mentioned, and in the section dealing with the literature of analytical chemistry we are indeed suprised that there is no mention of THE ANALYST or of the *Zeitschrift für analytische Chemie*, in both of which is to be found more information on analytical methods than anywhere else.

The article on naphthalene is almost a book in itself; it runs to 175 pages and is in three parts. We miss the name of Professor Wynne as its author, but there is a grateful acknowledgement to him from the new authors. It is a model of completeness and brings the subject up to date; there follow some pages on naphthenic acids, which are now so important in industry.

Another valuable article is on the moth-proofing of textiles; it is useful to have here the chemical equivalents of many trade names. Then there is information on nicotinic acid, its distribution and its determination by microbiological methods as well as by chemical methods. One could go on long drawing attention to all the "meat" to be found in this volume; it is full of good food and information on matters new and old. Whether the reader is an organic chemist, physical chemist, metallurgist, biochemist or analyst or whatever branch of chemistry is required, Thorpe, like our old friend Ranki-Poo, has a contribution to suit our every mood. Whether interested in milk, monel metal, nickel, nitrogen or the I.U.C. nomenclature or what you will, one cannot read Thorpe's contribution without profit even if it is on a familiar topic, and as a pointer to further sources of information it is most useful.

This volume is as invaluable as its predecessors, and can be cordially commended.

H. E. Cox

THE CHEMICAL CONSTITUTION OF NATURAL FATS. By T. P. HILDITCH, D.Sc., F.R.I.C., F.R.S. 2nd Edition. Pp. xiii + 554. London: Chapman & Hall, Ltd. 1947. Price 45s. net.

Our knowledge of the fats has been extended widely during the war years, developing generally on the lines that might have been expected from the later peace-time discoveries. In this new edition of his book, Professor Hilditch is able to record a considerable number of fresh analyses showing the nature and proportion of the constituent fatty acids of vegetable and land animal fats, including human fat, improvements in methods of investigating the glycerides of the more liquid and unsaturated fats, and a good deal of fresh information on individual fatty acids; he has responded to the welcome accorded to his earlier discussion of experimental technique by revising and expanding it; and he has provided a welcome index to the set of five separate indexes which deal with subjects, individual fats and waxes, plant families, natural fatty acids, and natural and synthetic glycerides.

The first edition of this work was hailed in many quarters as an outstanding contribution to our knowledge of the subject, an opinion amply confirmed by time. Professor Hilditch again merits our thanks for bringing his work as nearly up-to-date as possible by including all the more important contributions to the subject published before the end of 1945.

K. A. WILLIAMS

LIMIT TESTS FOR IMPURITIES. By F. REIMERS and K. R. GOTTLIEB. Pp. 198. Kopenhagen: Ejnar Munksgaard. 1946. Danish kronen 10·00.

This work represents Volume I of "Contributions from the Danish Pharmacopoeia Commission." Though it is in Danish, the title-page and preface are reproduced in English, and there is an English summary of 27 pages. The work records a thorough investigation of pharmacopoeial limit tests, *i.e.*, those tests in which limits for an impurity are established by means of comparison tests, having as its special object to determine whether these tests do in fact give a reliable basis for determining the permissible limits of impurity. The experiments showed that in most instances the methods previously used must be modified to some extent before they could be considered satisfactory from this aspect. In other instances, even though improvements were made, the final methods were not considered entirely satisfactory.

The work opens with a discussion of the formation of turbidities. It is interesting to note that the solubility of crystals of barium sulphate (and probably of other hard crystals such as those of calcium oxalate) is increased by 90 per cent. when the size of the crystals is reduced to 0·2 μ., whereas with soft crystals like lead iodide (and probably silver chloride) the solubility at 0·4 μ. is only increased by about 2 per cent. Kolthoff has calculated that barium sulphate crystals of diameter 0·04 μ. are about 1000 times more soluble than those of diameter over 1 μ. The significance of this phenomenon for the present application is obvious. Further, crystals of this type will rapidly grow larger at the expense of the smaller ones. Silver chloride, unlike barium sulphate, is thrown out in a colloidal form so that the effect described above does not enter into the precipitation, though coagulation may alter its appearance.

The tests investigated are those for chloride, heavy metals, ammonia, sulphate, calcium, magnesium, arsenic (with hypophosphite), potassium, sodium, nitrate, phosphate, cyanide, iron, other metals and carbonate. An abstract on p. 485 of this issue describes some of the methods recommended.

For chemists interested in tests of this type the book is well worth buying even for its English summary alone, as this gives not only recommended methods, but also a large number of explanatory footnotes. The standard of printing is high, though a stiff paper cover is not ideal for a work to which reference must continually be made. G. MIDDLETON

THE TECHNICAL AND SCIENTIFIC REGISTER

THE Technical Scientific Register is being carefully brought up to date by the Ministry of Labour and National Service, and the Ministry is anxious to make sure that no qualified chemist is omitted from the list. Members who for any reason did not receive the letter, and accompanying questionnaire, which has recently been issued are advised to apply for these to the Technical and Scientific Register, York House, Kingsway, London, W.C.2, or to any Regional Appointments Office of the Ministry and to furnish as fully as possible the information sought.

PURITY OF NICOTINIC ACID USED IN ASSAYS

SAMPLES of nicotinic acid prepared from β-picoline are liable to contain various proportions of *iso*-nicotinic acid. It has been established that *iso*-nicotinic acid is unavailable to *Lactobacillus arabinosus*, but that under certain conditions it may give rise to colour development with various amines. The presence of *iso*-nicotinic acid in any sample of nicotinic acid used as standard may therefore lead to discrepancy between chemical and microbiological results. The purity of the nicotinic acid used as standard is thus as important in microbiological as in chemical assays.

MAINTENANCE OF LABORATORY ANIMAL COLONIES

MEMBERS of the Biological Methods Group, and others interested in the production and care of laboratory animals, may like to know that the New York Academy of Sciences conducted a symposium in November, 1944, on the subject of animal colony maintenance. Nine papers were presented on various aspects of this subject, and these have since been published in the Annals of the Academy, Vol. **46**, 1–126. Copies of the collected papers bound together are available at \$1·50 per set.

BIOLOGICAL METHODS GROUP

THE Annual General Meeting of the Biological Methods Group will be held at 6 p.m. on Tuesday, December 16th, 1947, in the Rooms of the Chemical Society, Burlington House, London, W.1.

It will be followed at 6.15 p.m. by an Ordinary Meeting of the Group, at which the following papers will be presented and discussed: "A modified Method for the Microbiological Assay of Tryptophan, Methionine, Cystine and Tyrosine," by Dr. E. C. Barton-Wright and Mr. N. S. Curtis; "The Use of *Neurospora Crassa*, mutant 9185, for the Assay of Aneurine," by Mr. J. S. Harrison and Mr. E. J. Miller; "A Note on the Cup Method of Microbiological Assay and its Limitations," by Dr. W. F. J. Cuthbertson.

The Annual General Meeting will be confined to members of the Group, but guests will be very welcome at the Ordinary Meeting.

REPORTS OF THE ANALYTICAL METHODS COMMITTEE AND OTHER REPRINTS FROM "THE ANALYST" OBTAINABLE THROUGH THE EDITOR

The Reports of the Analytical Methods Committee and other Reprints listed below may be obtained direct from the Editor of THE ANALYST, 7–8, Idol Lane, London, E.C.3 (not through Trade Agents), at the price, except where otherwise stated, of 1s. 6d. to Members of the Society, and 2s. 0d. to non-Members. Remittances must accompany orders and be made payable to "Society of Public Analysts."

ANALYTICAL METHODS COMMITTEE REPORTS

The Reichert-Polenske-Kirschner Process. (Test for Butter Fat.)

Milk Products Sub-Committee:

Reports Nos. 1 and 2. Analysis of Condensed Milks.
Report No. 3. Analysis of Sweetened Condensed Milk in which the Sucrose has altered during Storage.
Report No. 4. Determination of Water, of Total Solids and of Fat in Dried Milk.

Sub-Committee on Dirt in Milk. Report. Determination of Dirt in Milk.

Report on the Determination of Total Solids in Fresh Liquid Milk.

Essential Oil Sub-Committee:

Report No. 1. Estimation of Cineole in Essential Oils. (1) Cajaput and Eucalyptus Oils.
Report No. 2. Physical Constants (1).
Report No. 3. Physical Constants (2).
Report No. 4. Interim Report on the Determination of Acetylisable Constituents in Essential Oils.
Report No. 5. Determination of Phenols in Essential Oils.
Report No. 6. Determination of Citral in Lemon Oil.
Report No. 7. Determination of Solubilities.
Report No. 8. Determination of Cineole in Essential Oils. (2) Camphor Oil. (3) Other Oils.
Report No. 9. Determination of Carvone and Menthone.
Report No. 10. Determination of Citronellal.
Report No. 11. Determination of Aldehydes other than Citronellal.
Report No. 12. Determination of Ascaridole.
Report No. 13. Determination of Esters.
Report No. 14. Solubility Test for Ceylon Citronella Oil. (Gratis.)

Sub-Committee on the Determination of Arsenic, Lead, etc. in Food Colouring Materials:

Report No. 1. Determination of Arsenic.
Report No. 2. Determination of Lead.
Report No. 3. Determination of Copper.

Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps:

Report No. 1. Determination of Unsaponifiable matter in Oils and Fats.
Report No. 2. Determination of Unsaponified Fat in Soap.
Report No. 3. Determination of Free Alkali in Soaps.
Report No. 4. Determination of Free Alkali and Silica in Silicated Soaps.
Report No. 5. Determination of Rosin in Soaps.
Report No. 6. Determination of Phenols in Soaps.

Poisons Sub-Committee appointed to investigate Methods of Assay for Various Substances appearing in the Poisons Schedules of the Poisons Regulations, 1935:

Report No. 1. Assay of Lobelia (*Lobelia Inflata*).
Report No. 2. Assay of Gelsemium
Report No. 3. Assay of Aconite.

Fluorine in Foods Sub-Committee:

Report on the Determination of Fluorine in Foods.
Addendum to above Report. (Gratis.)

Sub-Committee on Vitamin Estimations. Microbiological Panel:

Report on the Microbiological Assay of Riboflavine and Nicotinic Acid.

OTHER REPRINTS

Bibliography of the More Important Heavy Metals occurring in Food and Biological Materials
(For the ears 1929 to 1933 inclusive.)
Price 2s. 0d. to Members; 3s. 0d. to non-Members.

Methods of Analysis for the Purposes of the Cake and Flour Confectionery (Control and Maximum Prices) Order, 1942. (S.R. and O., No. 2103 of 1942.)

Lecture by Professor J. Heyrovský on "The Fundamental Laws of Polarography." Delivered at a meeting of the Society on October 31st, 1946.*