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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

AN open meeting of the North of England Section was held in Manchester on Saturday, 22nd June, 1946. The Vice-Chairman, Mr. C. H. Manley, who was accompanied by Mrs. Manley, presided over an attendance of thirty-two, including the President, Dr. G. W. Monier-Williams.

The earlier portion of the meeting was of an informal nature.

A resolution was unanimously passed expressing the continued loyalty of the Section to the Council and the Parent Society.

Dr. L. E. Campbell, F.R.I.C., gave a very interesting paper, illustrated by lantern slides, on "The History of Chocolate and Sugar Confectionery."

The Accurate Volumetric Determination of Zinc and Nickel Using Diphenylcarbazone as Indicator*

BY B. S. EVANS

I. ZINC

IN 1939 some work was published[1] dealing with a method for the volumetric determination of zinc, using an aged solution of diphenylcarbazide as indicator; in that method pyridine was used to obtain the correct *p*H value. The method worked well for a limited range of small amounts of zinc but attempts to extend this range to larger amounts showed that further investigation was desirable and that the method might prove rather uncertain in some circumstances. In especial the factor to be used for calculating the zinc seemed occasionally to "wander" somewhat unaccountably. From a long series of titrations undertaken to clear up the matter the following facts emerged:

(*a*) Addition of potassium ferrocyanide to a zinc solution may precipitate zinc ferrocyanide having one of two compositions, according to the *p*H of the solution. In what follows, the expression "M.R." (molecular ratio) is used to denote the number of atoms of zinc precipitated by 1 molecule of ferrocyanide. In the two compositions referred to above M.R. = 1·5 and 2·0.

The zinc ferrocyanide precipitated in acid solutions and used in the ordinary ferrocyanide titration with an external indicator has M.R. 1·5.

(*b*) At *p*H 6 and lower the M.R. 1·5 compound alone is formed; at *p*H between 6 and 8 the M.R. gradually increases from 1·5 to 2·0, *i.e.*, a mixture of ferrocyanides is precipitated. At *p*H 8 and above only the M.R. 2·0 compound appears to be formed, but slightly above *p*H 8 the ferrocyanide seems to begin to redissolve in the alkaline liquid, causing more ferrocyanide to be required to reach an end-point (probably a mass action effect).

(*c*) It is impracticable to aim at a M.R. 1·5 precipitate, as this is only formed completely at a *p*H too low to permit of the formation of the red colour with diphenylcarbazone.

(*d*) It is quite easy, by the use of ammonium nitrate and *N*/5 sodium carbonate, to produce a solution in which zinc can be titrated to the M.R. 2·0 end-point and the titration is practically theoretical over a long range (over 0·025 to 0·0001 g. of Zn). This simple method is preferable to the use of pyridine, which produces a *p*H that is not quite high enough.

(*e*) Potassium cyanide completely or partially destroys the red zinc colour. It is desirable to add cyanide to eliminate colour due to traces of nickel, which appear to be widespread. Subsequent addition of acetone has the effect of breaking down the zinc cyanide complex, while leaving that of nickel untouched, thus allowing the titration to go to its normal end-point. The acetone added in the original process, though put in for an entirely different

* Communication from the Armament Research Department formerly Research Department, Woolwich.

purpose, achieved this result. The amount prescribed must be adhered to; too much tends to reduce the colour, whilst too little does not completely remove the cyanide.

(*f*) It has been found preferable to use, as extractant, a mixture of equal parts of amyl alcohol and carbon tetrachloride in place of the chloroform originally recommended. Zinc diphenylcarbazone dissolved in this mixture reacts directly with ferrocyanide contained in the aqueous phase, thus eliminating the purpose for which acetone was originally added. It is still, however, necessary to add acetone for reasons given under (*e*). A volume of 20 ml. of solvent is better than the original 5 ml. where appreciable amounts of zinc are involved (say above 0·001 g.); the larger volume forms a less persistent emulsion with the precipitated zinc ferrocyanide and also the reagent colour is less pronounced. With this amount of solvent 0·3 ml. of the diphenylcarbazone solution is used. For amounts of zinc below, say, 0·001 g., where $M/1000$ ferrocyanide is used for titration, the volume of solvent should be 10 ml. and the amount of indicator solution 0·1 ml.

(*g*) Titration is performed in a 250 ml. stoppered colourless glass bottle, or, much preferable if obtainable, a stoppered Pyrex flask. (Glass containing zinc must *not* be used, as this zinc is very liable to be extracted.) It is necessary to have two such bottles or flasks, one for the sample and the other for a blank; the colours of the solvents are compared after each addition of the titrant and the end-point occurs when the two colours match or rather, at any rate with the larger amounts of zinc, when the colour in the sample flask becomes paler than the blank. This effect is probably due in part to adsorption of the colourant on the zinc ferrocyanide. As there is occasionally a tendency for the zinc ferrocyanide to adhere to the walls of the bottles it is desirable that these should be rinsed with sodium hydroxide solution before washing prior to a fresh titration. This for some unexplained reason applies as much to the blank as to the solvent bottle. The blank sometimes exhibits a tendency to fade after some hours and so should be prepared freshly each day. The sample, after titration, also shows a tendency (much more marked) to fade; this is presumably due to a small excess of ferrocyanide in solution being oxidized to ferricyanide, which compound seems to destroy the reagent. It has been found very much easier to compare the colours if the two bottles are gently inverted and held to the light upside down.

(*h*) The ferrocyanide standard keeps very well if not exposed to light (*e.g.*, in an amber glass bottle) but it must not be exposed to light more than is absolutely necessary. It can readily be standardized against standard zinc solution.

(*j*) Nickel, cobalt, copper, ferrous iron, cadmium and other metals give colours with diphenylcarbazone. The elimination of these interferences will be the subject of further papers.

On the basis of the foregoing observations the following method has been worked out.

METHOD—

Place the neutral solution (giving the faintest mauve shade to litmus paper) in one of the titration bottles; add to both bottles:

i. 20 ml. of 20 per cent. ammonium nitrate solution
ii. 15 ml. of $N/5$ sodium carbonate solution
iii. 4 drops of 10 per cent. potassium cyanide solution
iv. Water to make up approximately 150 ml.
v. 10 ml of acetone.

Shake both bottles and allow to stand for 15 minutes. Add to both bottles:

vi. 20 ml. (10 ml. for small amounts) of amyl alcohol - carbon tetrachloride mixture (1 : 1)
vii. 0·3 ml. (0·1 ml. for small amounts) of diphenylcarbazone solution (1·5 per cent. in alcohol).

Shake each bottle very vigorously for 15 seconds.

Titrate away the red colour in the solvent layer of the sample bottle with $M/100$ potassium ferrocyanide solution ($M/1000$ for small amounts), shaking vigorously for 15 seconds after each addition and allowing to settle long enough to permit comparison of the colours in the solvent layers. Allow the blank bottle meanwhile to stand on the bench, but if the solvent layer appears hazy shake again. Take as end-point the figure at which the red colour has entirely disappeared and the shades of colour in the two bottles are the same, but as a rule the depth of colour in the sample bottle will be less than that in the blank and, if it is not, an extra drop should be run in to make sure that there is no further change. Towards the

end of the titration the speed of removal of the red colour slows down considerably. Near the end-point the solvent layer must be allowed to settle completely and be free from bubbles before comparison is made; on the other hand, while the liquid is noticeably red or pink during shaking no period of settling is necessary. Comparison is best made by cautiously inverting both bottles so that the solvent runs down into the necks, and holding up to the light. Both bottles must be cleaned by rinsing with dilute sodium hydroxide solution and subsequent thorough washing before re-use. A final rinse with distilled water is necessary.

1 ml. of $M/100$ $K_4Fe(CN)_6 \equiv 0{\cdot}0013076$ g. of Zn.

Trials were made of the above process on amounts of zinc ranging from 0·0250 g. to 0·00010 g. For quantities between 0·0250 and 0·0020 g., titration was made with $M/100$ $K_4Fe(CN)_6$; below 0·002 g. $M/1000$ was used. Results are given in Table I. The molecular ratio, M.R. (*vid. sup.*), corresponding to each titration is given in the last column.

TABLE I

Zinc taken g.	Titration	Zinc found (calc. from M.R. 2·0 g.	M.R. calc. from titration
0·0250	19·08 ml. $M/100$ $K_4Fe(CN)_6$	0·02496	2·003
0·0230	17·55 ,, ,, ,,	0·02296	2·005
0·0210	16·05 ,, ,, ,,	0·02100	2·001
0·0190	14·55 ,, ,, ,,	0·01903	1·998
0·0170	13·00 ,, ,, ,,	0·01700	2·000
0·0150	11·45 ,, ,, ,,	0·01498	2·003
0·0130	9·95 ,, ,, ,,	0·01302	1·999
0·0100	7·65 ,, ,, ,,	0·01000	2·000
0·0080	6·05 ,, ,, ,,	0·00794	2·021
0·0060	4·55 ,, ,, ,,	0·00595	2·018
0·0040	3·05 ,, ,, ,,	0·00399	2·006
0·0020	1·55 ,, ,, ,,	0·00203	1·97
0·00100	7·72 ,, $M/1000$,,	0·001010	1·98
0·00090	6·85 ,, ,, ,,	0·000896	2·01
0·00080	6·15 ,, ,, ,,	0·000805	1·99
0·00070	5·35 ,, ,, ,,	0·000700	2·00
0·00060	4·60 ,, ,, ,,	0·000601	1·99
0·00050	3·83 ,, ,, ,,	0·000501	2·00
0·00040	3·05 ,, ,, ,,	0·000399	2·01
0·00030	2·40 ,, ,, ,,	0·000314	1·91
0·00020	1·50 ,, ,, ,,	0·000196	2·04
0·00010	0·75 ,, ,, ,,	0·000098	2·04

II. NICKEL

The ordinary volumetric method for nickel by cyanide titration leaves little to be desired, but for quantities much below 0·001 g. its sensitivity falls off rapidly and a colorimetric process has to be used. The colorimetric process in ordinary use[2] is fair, as colorimetric processes go, but it is lengthy and, equilibrium being very slowly established, it needs performing with care. The fact that nickel produces with diphenylcarbazone a red colour similar to that produced by zinc, and equally extractable with solvents,[1] makes possible a volumetric method of great range and accuracy, using diphenylcarbazone as indicator and cyanide as titrant. The procedure is similar to that described above for zinc, with the following differences.

(*a*) No addition of potassium cyanide or acetone is made.
(*b*) The extractant consists of 20 ml. of amyl alcohol alone.
(*c*) The titrating liquid is the cyanide solution used in the ordinary cyanometric titration of nickel (4·8 g. KCN + 2·3 g. of KOH per 1000 ml.) or dilutions thereof.
(*d*) For quantities of nickel below 0·0001 g. (for which a 100-fold dilution of the cyanide solution is required) a larger addition of sodium carbonate is desirable.

METHOD—

Take two titration bottles (*vid. sup.*), place the neutralised nickel solution (which must be free from the following ions: $Cu^{\cdot\cdot}$, $Cu^{\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Hg^{\cdot}$, $Hg^{\cdot\cdot}$, $V^{\cdot\cdot\cdot}$, $V^{\cdot\cdot\cdot\cdot}$, $Co^{\cdot\cdot}$) in one of them and a similar volume of water in the other. Add to each:

(i) 20 ml. of 20 per cent. ammonium nitrate solution
(ii) 15 ml. of $N/5$ sodium carbonate (for quantities of nickel below 0·0001 g. 50 ml. should be used)

make up each volume to between 100 and 150 ml. and add

(iii) 20 ml. of amyl alcohol
(iv) 0·3 ml. of diphenylcarbazone solution (1·5 per cent. in alcohol).

Shake each bottle vigorously and titrate away the red colour in the sample bottle with potassium cyanide solution (*vid. sup.*), shaking vigorously after each addition and allowing to settle, until the colours in the two solvents match. For amounts of nickel down to 0·001 g., the ordinary cyanide solution (1 ml. ≡ approx. 0·001 g. of Ni) may be used, down to 0·0001 g. ten-fold dilution of the cyanide is necessary and below 0·0001 g. hundred-fold dilution; the limit of visibility for titration is about 1 μg. As the cyanide solution alters slowly, standardisation is necessary; for the purpose of the table given below the strong solution was standardised in the ordinary way against standard silver solution, using potassium iodide as indicator, and it was assumed that dilution did not *per se* introduce any error.

The figures in Table II were obtained from titrations of known amounts of nickel by the above method.

TABLE II

Nickel taken g.	Titration ml.	Titrating solution	Factor	Nickel found g.	N/5 Na_2CO_3 added ml.
0·00992	9·70	KCN/1·0	1·023	0·00992	15
0·00893	8·77	,,	,,	0·00897	15
0·00795	7·80	,,	,,	0·00798	15
0·00695	6·90	,,	,,	0·00705	15
0·00597	5·90	,,	,,	0·00603	15
0·00498	4·85	,,	,,	0·00496	15
0·00397	3·80	,,	,,	0·00391	15
0·00297	2·90	,,	,,	0·00297	15
0·00198	2·00	,,	,,	0·00204	15
0·00099	1·00	,,	,,	0·00102	15
0·00100	9·90	KCN/10·0	1·010	0·00100	15
0·00090	9·05	,,	,,	0·000914	15
0·00080	7·85	,,	,,	0·000794	15
0·00070	6·95	,,	,,	0·000703	15
0·00060	5·95	,,	,,	0·000601	15
0·00050	4·95	,,	,,	0·000500	15
0·00040	3·95	,,	,,	0·000400	15
0·00030	3·05	,,	,,	0·000308	15
0·00020	2·10	,,	,,	0·000212	15
0·00010	1·10	,,	,,	0·000111	15
0·00010	10·8	KCN/100·0	0·926	0·000100	50
0·00009	9·7	,,	,,	0·000090	50
0·00008	8·7	,,	,,	0·000080	50
0·00007	7·7	,,	,,	0·000071	50
0·00006	6·4	,,	,,	0·000059	50
0·00005	5·4	,,	,,	0·000050	50
0·00004	4·3	,,	,,	0·000040	50
0·00003	3·2	,,	,,	0·000030	50
0·00002	2·1	,,	,,	0·000020	50
0·00001	1·1	,,	,,	0·000010	50

For the lowest amounts comparison was made by looking down through the coloured layers at a white tile.

III. DETERMINATION OF ZINC IN NICKEL PLATING BATHS

There is a tendency for zinc to accumulate in nickel plating baths; while negligible in the lower ranges, above a certain amount (say, 0·1 g. per litre) this zinc exerts a deleterious influence. There is therefore a need for a method of determining the zinc or, at any rate, for a test that will show if the limiting amount has been exceeded. As indicated in the above volumetric processes for zinc and nickel the nickel cyanide complex is sufficiently stable not to give a colour with diphenylcarbazone, while the zinc cyanide complex can readily be decomposed by acetone. On this basis it is quite simple to titrate a small amount of zinc in presence of a greatly preponderating amount of nickel; the borate, chloride, potassium and ammonium ions present exert no influence on the titration; as the bath is neutral there is no need for prior neutralisation. The following procedure has been worked out:

To 10 ml. of the plating bath solution add 10 ml. of 20 per cent. ammonium chloride solution, followed by 15 ml. of *N*/5 sodium carbonate solution; filter through closely packed

pulp into one of the titration bottles mentioned above, wash the filter four or five times with 5 per cent. ammonium chloride solution and discard it. Run in from a burette into the filtrate 10 per cent. potassium cyanide solution, shaking vigorously meanwhile. The nickel first precipitates as cyanide and then, with further addition, redissolves as the double cyanide. While the liquid remains turbid the cyanide may be run in rapidly, but as it begins to clear addition must be more cautious and, just before the end-point, drop by drop with intermediate vigorous shaking; the end-point is indicated by the liquid becoming bright. Add four drops of cyanide in excess, shake and allow to stand a minute or two; add 10 ml. of acetone, replace the stopper, shake vigorously and allow to stand for 15 minutes. At the end of this time add 20 ml. of the amyl alcohol - carbon tetrachloride mixture (*vid. sup.*) followed by 0·3 ml. of the diphenylcarbazone solution, shake vigorously for 15 seconds and titrate with *M*/100 ferrocyanide as given above under "Zinc."

As the titration is apt to be rather slow, and as what is usually needed is a test to indicate whether or not zinc is in excess of a certain amount, it is generally sufficient to run in ferrocyanide corresponding to this amount before adding the solvent mixture; then if on shaking with the indicator the solvent layer is coloured red there is an excess of zinc present which can, if necessary, be titrated. Thus: supposing 0·1 g. per litre is the limiting amount, one adds in this way 0·77 ml. of *M*/100 $K_4Fe(CN)_6$ to the liquid after the acetone treatment, then the solvent and the carbazone, shakes and observes the colour produced. When the quantities stated above are used

1·0 ml. of *M*/100 $K_4Fe(CN)_6 \equiv 0{\cdot}13076$ g. of zinc per litre.

The above method was tried on a nickel plating bath actually in use, with additions of various amounts of zinc. The composition of the bath was: nickel sulphate 240 g./litre, boric acid 30 g./litre, potassium chloride 19 g./litre.

Ten ml. quantities of this bath were used for each test. Results were as follows:

Zinc added g.	Titration ml. *M*/100 $K_4Fe(CN)_6$		Zinc found, corrected for blank g.	Zinc, g./litre	
	Actual	Corrected for blank		Added	Found
blank	0·42	—	—	—	—
0·00200	1·95	1·53	0·00200	0·200	0·200
0·00100	1·18	0·76	0·00099	0·100	0·099
0·00080	1·03	0·61	0·00080	0·080	0·080
0·00060	0·87	0·45	0·00059	0·060	0·059
0·00040	0·73	0·31	0·00041	0·040	0·041
0·00020	0·60	0·18	0·00023	0·020	0·023

In the above the "blank" was derived from the sample of plating bath used, but it is desirable that all chemicals used should be tested.

SUMMARY

Methods have been described for

(*a*) The volumetric determination of zinc and of nickel by a new process, each method being available for very low quantities and for a wide range of sample weight.

(*b*) The volumetric determination, without separation, of zinc in nickel plating baths.

(*c*) The detection of an excess of zinc over a given amount in nickel plating baths.

Thanks are due to the Director General of Scientific Research for permission to publish this paper.

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July, 1946

A Method for the Determination of Zinc in Copper Alloys and for the Separation of Zinc from Cadmium*

By B. S. EVANS

THERE are of course methods for the determination of zinc in copper alloys, but most of these are sufficiently long and involved to make it a common practice to determine the other components present and "take the zinc by difference." This is a bad principle; not only does it assume the accuracy of all other determinations, for which it provides no check, but it also ignores the possibility of the presence of some unusual constituent which has not been determined.

The method given below is based on certain principles which are either new or have hitherto not been used in copper-alloy analysis. A prolonged examination of the behaviour of the double cyanides of certain metals in presence of the sulphide radicle has brought to light the following facts:

(*a*) *Alkaline cyanides*—In absence of ammonium salts and with moderate excess of alkali cyanide and excess of alkali sulphide, if the liquid is boiled for 20 minutes and cooled, copper, nickel and cobalt remain in solution, and zinc, lead, cadmium and bismuth are completely precipitated.

I have for many years used this method, which gives a beautifully clean separation, in especial, of copper from zinc.

(*b*) *Ammoniacal cyanides*—Under conditions as in (*a*) but with a good excess of ammonia and ammonium salt present, if the liquid is heated just to vigorous boiling and then immediately cooled, the behaviour of the seven metals mentioned above is the same as in (*a*) with the exception that zinc now remains completely in solution.[1] The heating of the solution must be carefully controlled; cadmium in small amount does not readily precipitate from this solution until boiling temperature is reached; on the other hand, boiling with ammonium salts rapidly destroys the cyanide radicle, causing zinc sulphide to begin to precipitate. Liquids containing traces of zinc sulphide must be completely cooled before being filtered.

These separations appear to be clean; consequently if one starts with a solution of the seven metals, dissolves the precipitate from (*a*), after washing with 5 per cent. potassium nitrate solution, in diluted *aqua regia*, makes ammoniacal and carries out the precipitation (*b*) with a mixture of ammonium nitrate, potassium cyanide and sodium sulphide, the filtrate from the precipitate so obtained contains all the zinc and none of the other six metals.

(*c*) If excess of acetone is added to the filtrate containing the zinc a pure white precipitate is obtained after a certain period of standing. Time has not permitted any attempt to find out whether this is merely zinc sulphide allowed to precipitate by the destruction of the cyanide by the acetone, or whether it is a zinc mercaptide (the odour of the solution indicates that mercaptans are formed). Whatever its composition, this precipitate allows of all zinc, down even to very small amounts, being filtered off from the solution. It is to be noted that acetone precipitates also copper sulphide but not nickel sulphide from ammoniacal cyanide solution, though not so readily as it does zinc sulphide.

On these three reactions the following scheme for the determination of zinc in copper alloys is based. It must be noted that preliminary removal of manganese is desirable owing to the erratic behaviour of its sulphide, and that the solubilising effect of thiostannates on zinc sulphide in ammoniacal liquids makes it necessary to remove any tin in the early stages; this is sufficiently achieved by dissolving the alloy in nitric acid, "metastannic acid" not adsorbing zinc to any significant extent.

Iron in the alloys is quantitatively converted to ferrocyanide in the process, while aluminium goes into solution as aluminate; both are filtered off from the zinc after the first zinc sulphide precipitation. A series of experiments carried out to prove the accuracy of the separation of zinc from copper, given under (*a*) above, gave results shown in Table I (p. 461). In these experiments the separation was carried out as given under (*a*); the resulting zinc sulphide was dissolved in diluted *aqua regia*, the acid was neutralised and the zinc titrated with $M/100$ potassium ferrocyanide, using diphenylcarbazone as indicator[2] (*vid. inf.*).

* Communication from the Armament Research Department, formerly Research Department, Woolwich.

In formulating a procedure for the determination of zinc in all commercial copper alloys provision has to be made for the separation of several other metals besides copper. The great majority of these are dealt with by the (*a*) separation combined with certain routine procedures; if any cadmium is present, however, it will follow zinc through all the stages and will upset the titration, as it forms an intense colour which is not readily titrated away under the conditions laid down. In presence therefore of even a very small amount of

TABLE I

Copper taken g.	Zinc taken g.	Titration $M/100$ $K_4Fe(CN)_6$ ml.	Zinc found g.	Per cent. of zinc: Added	Per cent. of zinc: Found
0·100	nil	nil	nil	nil	nil
0·100	0·0429	32·70	0·0428	30·03	29·96
0·100	0·0333	25·35	0·0333	24·99	24·99
0·100	0·0250	19·20	0·0251	20·02	20·10
0·100	0·0125	9·55	0·0125	11·11	11·11
0·100	0·00525	4·15	0·00542	4·99	5·15

cadmium it is necessary to superimpose the separation given under (*b*) followed by (*c*). This has also the merit of finally separating the trace of lead always remaining in solution after the lead sulphate separation. In absence of cadmium, however, this lead does not matter, as it does not interfere with the titration. The following procedure has been found satisfactory for all kinds of copper alloys so far tested.

METHOD

It is essential that all glassware used should be of some glass (e.g., *Pyrex*) *which does not contain zinc in its formula.* Some resistance glasses contain considerable amounts of zinc.[3]

Dissolve 1 g. (or other convenient amount) of the alloy sample in diluted nitric acid (sp.gr. 1·2) and evaporate to 2–3 ml.; dilute to about 50 ml. with cold water, add about 10 ml. of 20 per cent. sodium sulphate solution and cool completely. Filter into a 100 ml. measuring flask and wash the filter with 2 per cent. sulphuric acid; discard the filter, make up the filtrate to the mark and mix. Pipette off the required aliquot (the expected zinc should be between 0·002 and 0·035 g.) and neutralise it with dry sodium carbonate added a little at a time, with vigorous stirring, until the copper precipitates as blue-green carbonate and carbon dioxide ceases to be evolved in any large amount. Run in 10 per cent. potassium cyanide solution from a burette until solution is practically complete and the liquid has a yellow colour; in presence of much copper (*i.e.*, with a large aliquot due to low zinc) it is best first to remove the greater part of the insoluble matter with saturated potassium cyanide, run in from a beaker, to avoid an excessive volume of liquid. In presence of much manganese the solution may not become quite bright and may have a brownish colour but the end-point is sufficiently obvious and a slight excess of cyanide does not matter, though towards the end additions should be of not more than 2 drops at a time. When the cyanide precipitate has been completely dissolved run in an excess of 10 ml. of 10 per cent. potassium cyanide solution. heat nearly but not quite to boiling and add 20 ml. of 20 per cent. sodium hydroxide solution followed by 5 ml. of 20 vol. hydrogen peroxide; boil briskly for 5 minutes, filter off any precipitated manganese dioxide and wash with hot water. Add to the filtrate 10 ml. of 10 per cent. sodium sulphide solution, boil vigorously for 20 minutes, cool and filter off the precipitated zinc sulphide. Rinse-in and wash the precipitate with a mixture of 10 ml. of 10 per cent. potassium cyanide solution, 10 ml. of 10 per cent. sodium sulphide solution and 20 ml. of 20 per cent. potassium nitrate solution in 3–4 small quantities, then two or three times with 5 per cent. potassium nitrate solution, and finally four times with 5 per cent. ammonium nitrate solution. In absence of cadmium this completes the necessary separation of the zinc.

If cadmium is present, pour 20 ml. of diluted *aqua regia* ($25\,HNO_3 + 75\,HCl + 100\,H_2O$ by vol.) into the precipitation flask and heat to boiling, transfer the funnel containing the sulphide precipitate to a clean flask and pour the boiling acid through the filter in two portions, taking care that all the precipitate is attacked. Rinse-in the flask and wash the filter with hot water; add 20 ml. of 20 per cent. ammonium nitrate solution to the filtrate, make strongly ammoniacal and add 30 ml. of 10 per cent. potassium cyanide solution followed by 10 ml of 10 per cent. sodium sulphide solution; heat *just* to vigorous boiling (not more), cool completely at once and filter without delay; wash with 5 per cent. ammonium nitrate solution. Add

to the filtrate 60 ml. of acetone, shake well and allow to stand; if at the end of 10 minutes no haze of zinc sulphide is shown* add a further 20 ml. of acetone and allow to stand again; fifteen minutes after the haze begins to develop add a little filter pulp, shake well, allow to stand five minutes cold and fifteen minutes on the steam bath with occasional shaking; then cool completely. Filter off the pulp and zinc sulphide on a closely pressed pulp filter and wash with 5 per cent. ammonium nitrate solution.

TABLE II

Sample	Weight taken g.	Titration $M/100$ $K_4Fe(CN)_6$ ml.	Zinc on certificate %	Zinc found %	Process used
Bur. of Stds. Mn Bronze No. 62 *Certificate* Cu 59·07 Sn 0·82 Zn 35·06 Pb 0·56 Mn 1·59 Ni 0·64 Fe 1·13 Si 0·02 Al 1·13	1·0033 / 10	26·80	34·90–35·12	34·97	First separation only
Bur. of Stds. Cast Bronze No. 52 *Certificate* Cu 88·33 Sb 0·16 Sn 7·90 Ni 0·13 Zn 1·89 Fe 0·12 Pb 1·52	0·4016	5·65	1·86–1·94	1·84	First separation only
Ditto with addition of 1·0% Cd	1·002 / 2	7·20	1·86–1·94	1·88	Full separation
Bur. of Stds. Phosphor Bronze Bearing Metal No. 63 *Certificate* Cu 78·05 Sb 0·55 Sn 9·91 Zn 0·48 Pb 9·74 Fe 0·27 P 0·62 As 0·19	2·00	7·70	0·45–0·52	0·50	First separation only
Ditto with addition of 1·0% Cd	2·00	6·90	0·45–0·52	0·45	Full separation
Bronze values analysed in A.R.D. No. 2 Cu 57·84 Mn 1·15 Pb 0·90 Sn 1·09 Fe 0·95	0·6085 / 10	—	*Zinc by difference* 38·07	38·25	First separation only
Ditto No. 3 Cu 58·43 Mn 0·63 Pb 0·47 Sn 1·03 Fe 1·07	0·5521 / 10	—	38·37	38·05	First separation only

Whether or not the additional separation from cadmium has been necessary, we now have a filter containing all the zinc in the form of zinc sulphide free from all interfering metals. The zinc is determined by the titration method described in an earlier paper.[2] This method requires two similar white glass stoppered bottles (capacity 250 ml.) or, much better if obtainable, two Pyrex flasks with ground-in stoppers (glass containing zinc must *not* be used). Transfer the funnel containing the filter with the zinc sulphide to one of these bottles, place 20 ml. of diluted *aqua regia* (*vid sup.*) in the vessel used for the precipitation of the zinc sulphide

* 0·001 g. of zinc treated as above, and in a volume of 430 ml., showed a distinct haze at the end of 10 minutes. The haze gradually thickened to a turbidity during the next 10 minutes.

and another 20 ml. of the same batch of *aqua regia* in the second bottle. Heat to boiling the *aqua regia* in the precipitation flask and pour it in two portions over the filter, taking care that the precipitate is completely attacked; rinse-in the precipitation vessel and wash the filter four times with hot water; discard the filter. The two titration bottles contain respectively:

(*a*) The zinc dissolved in *aqua regia* and diluted with water.
(*b*) The blank; *aqua regia* only.

Dilute the acid in the blank to approximately the same volume as in the experimental bottle, add a fragment of litmus paper to each bottle and then diluted ammonia (1+1) until, after thorough mixing, each paper turns blue. Add from a dropping bottle diluted nitric acid (sp.gr. 1·2) till each paper just turns red again and cool completely. Add diluted ammonia (1+1) to each, drop by drop with thorough shaking, until the litmus papers assume the first shade of lilac; then add to each 15 ml. of $N/5$ sodium carbonate followed by 4 drops of 10 per cent. potassium cyanide solution and finally, after shaking, by 10 ml. of acetone; stopper, shake and allow to stand 15 minutes. Add to each bottle 20 ml. of a 1 : 1 mixture of amyl alcohol and carbon tetrachloride followed by 0·3 ml. of a 1·5 per cent. solution of diphenylcarbazone in alcohol; shake each violently for 15 seconds. The solvent in the sample bottle should now have a red colour of depth proportional to the zinc present, that in the blank should be orange brown. Titrate away the red colour of the sample with $M/100$ potassium ferrocyanide, shaking violently after each addition until the red colour has completely disappeared and the solvent has the same tint as that in the blank, though probably paler; if the shades seem to match exactly it is desirable to add another drop of the titrant to see if any further removal of colour takes place. Exact matches are sometimes obtained with very minute amounts of zinc but almost invariably the fully titrated solution is paler than the blank, probably owing to some adsorption of the colour on the precipitated zinc ferrocyanide. Near the endpoint the emulsified solvent should be allowed to clear completely before matching, which is best performed by cautiously inverting both bottles and holding them up to the light upside down.

$$1 \text{ ml. of } M/100 \ K_4Fe(CN)_6 \equiv 0{\cdot}0013076 \text{ g. of zinc.}$$

A number of determinations were carried out by this method on U.S. Bureau of Standards' samples, also on previously analysed samples with and without addition of cadmium. The results shown in Table II were obtained (see p. 462).

Separation of zinc from cadmium

The ordinary separation of zinc from cadmium by precipitating the latter as cadmium sulphide by hydrogen sulphide from a dilute sulphuric acid solution of regulated acidity leaves something to be desired. My experience is that with a single precipitation some zinc is always carried down with the precipitate. It seemed desirable to try out the method given in this paper with known and varying amounts of zinc and cadmium. The method used was exactly that given in the process, including the addition of 20 ml. of diluted *aqua regia*; use of 30 ml. of 20 per cent. ammonium nitrate solution instead of 20 ml. of *aqua regia* + 20 ml. of ammonium nitrate solution gave a slightly low result (0·0250 g. added; 0·0245 g. recovered) presumably owing to slight adsorption. The zinc was determined as described in the paper; the cadmium sulphide was redissolved and reprecipitated in the usual manner from dilute sulphuric acid and weighed as cadmium sulphate. Results are shown in Table III.

Table III

	Zinc		Cadmium		
	Taken g.	Found g.	Taken g.	Found g.	
(*a*)	0·0250	0·0249	0·0250	0·0253	Tentative
(*b*)	0·0250	0·0249	0·0010	0·0017	* results
(*c*)	0·0100	0·0098	0·0250	0·0255	only
(*d*)	0·0010	0·00099	0·0250	0·0250	

* Cadmium results (*a*), (*b*) and (*c*) had to be heavily corrected owing to unsuspected contamination of the distilled water; they are therefore submitted as approximate only.

These figures show that the method given in this paper works satisfactorily. If the method is to be applied to separations of zinc from cadmium under other circumstances it must be

pointed out that an adequate amount of ammonium salt is a *sine qua non* and that if the prescribed 20 ml. of diluted *aqua regia* is not added a corresponding amount of ammonium nitrate must be introduced.

The method works equally cleanly for separation of zinc from lead and presumably from bismuth, but time did not allow of the latter separation being tested quantitatively.

SUMMARY

(*a*) An examination has been made of the behaviour of the double cyanides of certain metals in presence of the sulphide ion.

(*b*) A method has been worked out, based on (*a*), for the complete separation of zinc from other heavy metals.

(*c*) A method has been worked out, based on the removal of cyanide by acetone for the complete recovery of zinc from the filtrate from (*b*).

(*d*) The methods of (*b*) and (*c*) have been applied to the determination of zinc in copper alloys.

(*e*) Demonstration has been made of the complete separation of zinc from cadmium in one precipitation.

Thanks are due to the Director General of Scientific Research for permission to publish this paper.

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Spot-Tests for the Detection of Alloying Elements in Aluminium- and Magnesium-Base Alloys*

BY B. S. EVANS AND D. G. HIGGS

PART I

ALUMINIUM-BASE ALLOYS

THE tests described below follow the same line of approach as those described in an earlier paper[1] for the detection of alloying elements in steel. Aluminium offers a very wide range of alloys and almost as many alloying elements as does steel. The following elements have been detected: copper, magnesium, zinc, manganese, tin, iron, nickel, titanium, antimony, bismuth, lead and chromium.

Apparatus—The apparatus required is exactly as before, *i.e.*, (*a*) short lengths of narrow glass tubing drawn out into fine long jets, (*b*) short drawn-out glass rods to act as stirrers, (*c*) a porcelain spot-plate and (*d*) a mild steel plate (titanium-free).

THE TESTS—As far as possible reagents and solution mixtures already employed for steel spot-testing are used and, where possible, exactly the same procedure. A great variety of samples have been collected, so that each element has been tested for in as many different surroundings as possible. Our aim, as before, has been to make every test specific and unambiguous. Compositions of the trial alloys are given in Table I and the numbers at the end of each test refer to that Table.

It is very important that for each test the surface of the sample be thoroughly cleaned by rubbing with a fine emery paper (Grade 1G or similar) *immediately* before the reagents are applied; the reason for this is the rapidity with which the aluminium surface becomes covered with a protective layer of very resistant oxide.

Only five of the following tests involve removal of the test drop from the surface of the sample; they are those for iron, titanium, antimony, lead and chromium.

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

(I) Copper

Reagents—(*a*) Sodium hydroxide (20%).
(*b*) Mixture of α-benzoin-monoxime (saturated solution in alcohol), 10 vols.; diluted ammonia (1+1), 20 vols.; citric acid solution (50%), 5 vols.

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave to react for 5 minutes. Wash off the drop with water and dry the specimen with an acetone wash. Add to the stain, resulting from the previous drop, 2 drops of (*b*) and leave for 5 minutes. In presence of copper a dirty green precipitate will form almost immediately, but with small amounts of copper the green precipitate may take about 5 minutes to develop. In absence of copper a white deposit will be observed due to precipitation of α-benzoin-monoxime as the alcohol evaporates. If in doubt as to the formation of the green precipitate from small amounts of copper, add a further 2 drops of (*b*) and again leave for 5 minutes.

Tried on: Samples Nos. 2, 14, 13, 15, 34, 35, 36, 37, 38, 39—Copper present; all gave positive results.
Nos. 40, 41, 42, 4, 8, 17, 21, 22, 23—Copper below 0·03 per cent. and all results negative.

(II) Magnesium

Reagents—(*a*) Bromine water (saturated solution).
(*b*) Quinalizarin solution (0·02% in 5% sodium carbonate solution); freshly prepared.
(*c*) Mixture of sodium hydroxide solution (5%), 1 vol.; potassium cyanide solution (10%), 1 vol.

Method—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave until decolorised. Add 2 drops of (*b*) followed by 3 drops of (*c*), stir the whole thoroughly with a pointed glass rod and then leave to react. In presence of large amounts of magnesium, say, over 1 per cent., an immediate blue precipitate will be seen floating at the top of the drop; down to about 0·4 per cent. magnesium shows up after about 1 minute and 0·1 per cent. shows after about 10 minutes. In absence of magnesium the colour of the drop remains purple (this is the colour of the reagent) for some little time and then slowly changes to a mauve and remains that colour. (This colour may *appear* to darken and is due to a deposit on the surface of the sample as a result of attack by reagent mixture (*c*).)

When the magnesium is expected to be low it is not advisable to take the early reactions as indicative of its presence since the purple colour of the drop and the somewhat vigorous gassing can be very deceptive to the naked eye.

Tried on: Samples Nos. 23, 24, 17, 18, 16, 19, 21, 20, 9, 11, 12, 25, 27—Magnesium present; all gave positive results.
Nos. 26, 4, 6, 7, 8, 1, 22—Magnesium below 0·02 per cent. and all results negative.

(III) Zinc

Reagents—(*a*) Sodium hydroxide solution (5%).
(*b*) Mixture of ammonium chloride solution (20%), 1 vol.; potassium iodide solution (4%), 1 vol.
(*c*) Mixture of pyridine nitrate (buffer solution),* 1 vol.; diphenylcarbazone solution (1·5% in alcohol),† 1 vol. Freshly prepared.

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave to react for at least 5 minutes. Add 2 drops of (*b*), stir the drop well and then leave for 1 minute. Add

* The pyridine buffer *must* be prepared from high grade pyridine; the water content of the pyridine is immaterial, but the impurities in many of the so-called "pure" pyridines on the market destroy the effectiveness of reagent (*c*) and make it valueless. Suitable pyridine has been obtained from B.D.H. and Hopkin and Williams. The buffer is prepared by diluting 300 ml. of pyridine to 1500 ml. with water, adding 20 ml. of concentrated nitric acid, heating to boiling and cooling. It is desirable to test reagent (*c*) if prepared from untried chemicals; with a solution of lead nitrate it should give a cherry-red colour. Mixture (*c*) must be made up fresh daily.

† This solution can be made up direct from the solid diphenylcarbazone; it has been found to work just as well as the "aged" solution made up from diphenylcarbazide, mentioned in our earlier paper; it may also be used for the vanadium test, described in the same paper (XII, p. 79) with equally good results.

6 drops of (*c*) and stir again. In presence of zinc an immediate violet precipitate is produced which is quite heavy for 3 per cent. of zinc and appears to be very stable. All other alloys give a salmon-pink colour on mixing. (If copper present is more than, say, 2 per cent. it will slowly react with the diphenylcarbazone to give a fine powdery purple precipitate. This slow reaction of copper, however, does not interfere with the observation of the zinc reaction, which is immediate.)

Tried on: Samples Nos. 22, 18, 26, 8, 7—Zinc present; all gave positive results.
Nos. 14, 11, 4, 15, 10, 16, 23, 24, 20, 27, 12, 19, 2, 17, 21—Zinc absent or <0·06 per cent. and all results negative.

(IV) Manganese

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Nitric acid (sp.gr. 1·20).
(*c*) Sodium bismuthate (solid).

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave to react for 5 minutes. Wash off the drop with water and dry the specimen with an acetone wash. Add 2 drops of (*b*) and allow to react until the blackish spot, if any, resulting from the previous drop, has dissolved. Add a little reagent (*c*) from the tip of a pen-knife blade and stir well into the drop. In presence of manganese a purple colour of permanganic acid is produced. Manganese as low as 0·09 per cent. gives a faint pink colour. In absence of manganese the liquid of the drop remains colourless.

Tried on: Samples Nos. 14, 13, 34, 36, 35, 12, 21, 22, 26, 27, 30—Manganese present; all gave positive results.
Nos. 2, 15, 37, 38, 39, 40, 41, 42—Manganese below 0·02 per cent. and all results negative.

(V) Tin

Reagent—(*a*) Mixture of phosphoric acid (syrupy), 1 vol.; diluted sulphuric acid (1+3), 2 vols; sulphurous acid (saturated solution), 2 vols; potassium cobalticyanide solution (10%), 2 vols.

Method—Place 1 drop of the reagent mixture (*a*) on the thoroughly cleaned surface and leave to react. In presence of tin a yellow precipitate will form after a few minutes; in absence of tin the drop of solution remains water-white in colour. (In presence of large amounts of zinc a white precipitate of zinc cobalticyanide will form, or, with over 5 per cent. of copper, the light blue precipitate of copper cobalticyanide). On allowing the drop to dry, a black deposit forms on the surface of the sample when tin is present—two samples only did not show this black deposit, they were Nos. 23 and 24; here the only metals absent, which were common to all the other samples tested, were copper and iron. All samples not containing tin dried without the black base.

Tried on: Samples Nos. 26, 9, 10, 23, 24, 25, 15, 27—Tin present; all gave positive results.
Nos. 18, 20, 11, 4, 21, 16, 14, 17, 19—Tin absent and all results negative.

(VI) Iron

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Diluted hydrochloric acid (1 in 10).
(*c*) Hydrogen peroxide (20 vols.).
(*d*) Ammonium thiocyanate solution (10%).

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface* and leave to react for 5 minutes. Wash off the drop with water and dry the specimen with an acetone wash. Add, to the stain resulting from the previous drop, 2 drops of (*b*) and leave for 1–2 minutes; then transfer, by means of a capillary tube, to the well of a porcelain spot-plate. Add to the transferred solution 3 drops of (*c*) followed, after thorough stirring with a pointed glass rod, by 3 drops of (*d*). Above 0·7 per cent. of iron an intense red coloration is produced immediately; 0·5–0·7 per cent. gives a deep red; 0·3–0·5 per cent. gives a red, 0·1–0·3 per cent. a

* Since the test is very delicate and traces of iron are easily picked up, a fresh strip of emery paper must be used for cleaning each sample.

salmon-pink and less than 0·1 per cent. gives varying intensities of shell-pink colours. The ferric thiocyanate colour fades slowly.

Tried on: Samples Nos. 31, 32, 26, 19, 14, 33, 16, 27, 9, 12, 21, 25, 20, 13, 30, 15, 22, 18, 29, 23, 28, 24—Iron present; all gave positive results.
No. 1 and a sample of very pure aluminium gave only a very slight shell pink colour.

In absence of zinc the following may be employed as a confirmatory test for iron, but it was found to fail amost completely when large amounts of zinc were present in the sample, the latter being preferentially precipitated.

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Diluted hydrochloric acid (1 in 10).
(*c*) Potassium ferricyanide solution (1·5% in 10% acetic acid).

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave for about 5 minutes. Wash off the drop with water and dry the sample with an acetone wash. Add 1 drop of (*b*) followed by 2 drops of (*c*), stir and leave to react. In presence of iron a blue coloration or precipitate will be observed. The test is very sensitive, and even small amounts of iron will be indicated after some standing; as an alloying element, however, iron is generally present at between 0·3 and 1·0 per cent. so a heavy blue precipitate will generally be given.

(VII) Nickel

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Mixture of citric acid solution (50%), 2 vols; diluted phosphoric acid (1 in 20), 2 vols.; nitric acid solution (sp.gr. 1·20), 1 vol.
(*c*) Mixture of diluted ammonia (1+1), 2 vols.; dimethylglyoxime (saturated solution in alcohol), 1 vol.

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave to react for 5 minutes. Wash off the drop with water and dry the sample with an acetone wash. Add 4 drops of (*b*) to the stain resulting from the previous drop and leave for 10 minutes. Add 6 drops of (*c*) and stir well. (All alloys containing iron will develop a reddish coloration which is easily dispelled by either stirring the drop or adding a little more of reagent (*c*).) In presence of nickel an almost immediate red precipitate of nickel glyoxime is produced. With as little as 0·2 per cent. of nickel the precipitate can be plainly seen floating on the sample. No precipitate is given in absence of nickel.

If in doubt transfer the solution, by means of a capillary tube, to the centre of a disc of 12·5 cm. No. 541 filter paper, adding the solution dropwise; when the additions are completed wash the paper with 2 or 3 drops of water added successively to the centre, whereupon any nickel precipitate will be plainly visible against the white background of the paper.

Tried on: Samples Nos. 16, 39, 19, 38, 37, 26, 27, 31—Nickel present; all gave positive results.
Nos. 2, 14, 13, 15, 1, 4, 8, 12, 21, 30—Nickel below 0·06 per cent. and all results negative.

(VIII) Titanium

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Hydrochloric acid (5% solution saturated with bromine).
(*c*) Chromotropic acid (5% solution in 10% HCl).
(*d*) Stannous chloride (5% solution in 10% HCl).

Method—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave for about 5 minutes. Wash off the drop with water and dry the sample with an acetone wash. Add to the stain from the previous drop 2 drops of (*b*) and leave until it has become decolorised; then transfer the drop, by means of a capillary tube, to a cleaned mild steel plate. Add to the transferred drop 2 drops of (*c*) followed by 2 drops of (*d*) and stir thoroughly. In presence of titanium a reddish-brown coloration appears in the drop after about 5–10 minutes. Between 0·05 and 0·09 per cent. of titanium the colour is a light brown with a tinge of red;

above 0·09 per cent. it is brownish red. In absence of titanium the drop slowly becomes light brownish-green. It may be necessary to allow the sample to become almost dry before a definite reaction can be noted when titanium is low.

Tried on: Samples Nos. 31, 32, 21, 19, 33, 26—Titanium present; all gave positive results.
Nos. 16, 9, 12, 24, 23, 14, 27, 15, 4, 13, 20, 22, 1—Titanium absent and all results negative. (Sample No. 22 contains 0·03 per cent. but it is probably below the limit of identification.)

(IX) Antimony

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Mixture of citric acid solution (50%), 1 vol.; bromine water (saturated solution), 1 vol.
(*c*) Diluted hydrochloric acid (1 in 10).
(*d*) Sodium hypophosphite (solid).
(*e*) Copper foil (approx. 3/16 inch square).

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave for 5 minutes. Wash off the drop with water and dry the sample with an acetone wash. Add to the stain from the previous drop 4–6 drops of (*b*) and allow to react until the bromine colour has all but gone; then quickly transfer, by means of a capillary tube, to a tall-form beaker (60 ml.). Add to the drops in the beaker 10 ml. of (*c*) followed by approximately 0·5 g. of (*d*). (Prepare (*e*) by treating with a little warm nitric acid (sp.gr. 1·20) until it is quite clean; wash in running water.) Drop the cleaned (*e*) into the beaker without touching the copper with the fingers, boil the solution slowly until the volume has been reduced to the point where the salts begin to crystallise, cool and dilute with cold water. In presence of antimony a purple deposit will be seen on the copper. 0·50 per cent. of antimony gives a heavy purple deposit. As little as 0·05 per cent. gave a faint purple coloration with the two samples Nos. 9 and 10. It was found that bismuth did not give a deposit when treated as above (Nos. 11, 12 and 20 containing 0·48, 0·72 and 0·19 per cent. of bismuth respectively).

Tried on: Samples Nos. 15, 25, 27, 26, 9, 10—Antimony present; all gave positive results.
Nos. 11, 12, 4, 22, 16, 32, 23, 21, 20—Antimony absent and all results negative.

(X) Bismuth

Reagents—(*a*) Mixture of potassium cyanide solution (10%), 1 vol.; sodium hydroxide solution (20%), 1 vol.
(*b*) Mixture of nitric acid (sp.gr. 1·20), 1 vol.; potassium cobalticyanide solution (10%), 1 vol.; urea solution (10%), 1 vol.
(*c*) Mixture of potassium iodide solution (4%), 1 vol.; antipyrine solution (1% in water), 1 vol.
(*d*) Potassium cyanide solution (10%).

Method—Place 1 drop of (*a*) on the thoroughly cleaned surface and leave to react for 5 minutes. Wash off the drop with water and dry the specimen with an acetone wash. Add, to the stain from the previous drop, 2 drops of (*b*) and leave for 5 minutes. (In presence of large amounts of zinc a white precipitate of zinc cobalticyanide will develop, or in presence of more than, say, 5 per cent. of copper, a slight precipitate of the blue copper cobalticyanide.) Add 2 drops of the reagent mixture (*c*) and stir. In presence of bismuth an immediate orange precipitate develops. Copper tends to form a slight brown precipitate after a few minutes but this is easily destroyed by addition of 1 drop of (*d*); the bismuth colour is not destroyed and the orange precipitate remains after half an hour's standing.

Tried on: Samples Nos. 11, 12, 20—Bismuth present; all gave positive results.
Nos. 9, 10, 4, 21, 22, 26, 25, 15, 14, 16, 18, 27, 23, 24—Bismuth absent and all results negative.

(XI) Lead

Reagents—(*a*) Sodium hydroxide solution (20%).
(*b*) Mixture of acetic acid (glacial), 1 vol.; chromic acid solution (10%), 1 vol.
(*c*) Acetic acid solution (10%).
(*d*) Mixture of potassium cyanide solution (1%), 9 vols.; dithizone solution (0·1% in chloroform), 1 vol. The mixture is freshly prepared before use.

Method—Place on the thoroughly cleaned surface sufficient (*a*) so that, when it is spread out, the whole surface is covered with the reagent and leave for about 5 minutes. Wash off the reagent with running water and dry the specimen with an acetone wash without further touching the surface with the fingers. Soak a piece of fine-grained filter paper of the required size and shape in (*b*), drain with its lower edge touching a piece of dry filter paper and apply it to the prepared surface of the alloy under test. Smooth out gently with the fingers to remove air bubbles, taking care not to move the paper on the specimen; press down firmly all over with a wad of dry filter paper. Leave for 5 minutes with a thin sheet of glass placed on the sample to prevent the paper being lifted from the surface of the sample by the bubbles of gas being evolved. Strip off the paper and transfer it to a beaker containing (*c*) and leave until the chromic acid has apparently all dissolved from the paper; then transfer to another beaker and wash well (say, for 2–3 min.) in running water. Transfer the paper again to a beaker containing (*d*), which has been thoroughly shaken, and leave, with occasional shaking, for 15 minutes. Again wash the paper in running water, drain, spread out on a glass plate and allow to dry.

Lead is indicated by red spots on a white background, the position of the spots indicating the distribution of the lead; in absence of lead the paper is white. The results, however, although quite distinctive, are not so good as those obtained from steels of similar lead contents; this is probably due to the lesser solubility of the aluminium alloys in the reagents employed.

Tried on: Samples Nos. 4, 6, 5, 3, 20, 26—Lead present; all gave positive results.
Nos. 14, 10, 12, 16, 1, 8, 15, 21, 22, 23—Lead absent and all results negative.

(XII) Chromium

Reagents—(*a*) Mixture of concentrated hydrochloric acid, 1 vol.; hydrogen peroxide (20 vols.), 1 vol.
(*b*) Mixture of sodium hydroxide solution (20%), 1 vol.; hydrogen peroxide (20 vols.), 1 vol.
(*c*) Mixture of diluted sulphuric acid (1+3), 1 vol.; diphenylcarbazide solution (1% in pure glycerol),* 1 vol.; ammonium phosphate solution (10%), 1 vol.; acetic acid (glacial), 1 vol.

Method—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave to react for 10 minutes. Wash off the drop on to a small clean watch-glass with 2 drops of distilled water. Add 6 drops of (*b*), stir well and leave for 2–3 minutes. (The mixed solution *must* be alkaline at this stage.) Take up the solution, by means of a capillary tube, and transfer, dropwise, to the centre of a disc of close-grained filter paper supported on the open mouth of a beaker. Repeat, if necessary, until all the liquid has been transferred from the watch-glass to the filter paper. Allow to spread completely and then add a succession of drops of (*c*) round the edge of the wet patch. In presence of chromium purple bands of colour are produced, within 1–2 minutes, where the reagent (*c*) penetrates into the solution of the alloy. No coloration is produced in absence of chromium. Any colour produced on drying of the patch is due to reactions other than that of chromium; pure aluminium itself gave an orange colour where reagent (*c*) had been added and all papers showed a slight coloured crescent, varying from purple to violet, after about 8–10 minutes.

Tried on: Samples Nos. 21, 22 (the only two samples available)—Chromium present; both gave positive results.
Nos. 43, 18, 26, 8, 12, 15, 4, 31, 16, 9, 27, 23, 14, 19—Chromium absent and all results negative.

* Diphenylcarbazide solution in glycerol keeps its properties indefinitely and has been found, when mixed with acetic acid and sulphuric acid, to give excellent results for the spot-testing of chromium in steel.

TABLE I—ALUMINIUM ALLOYS

Percentages

No.	Mark	Cu	Mg	Zn	Mn	Si	Sn	Fe	Ni	Ti	Sb	Bi	Pb	Cr
1	Pure	—	—	—	—	—	—	—	—	—	—	—	—	—
2	Mod. Dural.*	10	10	—	—	—	—	—	—	—	—	—	—	—
3	EX.1*	—	—	—	—	—	—	—	—	—	—	—	0·24	—
4	EX.2*	—	—	—	—	—	—	—	—	—	—	—	1·11	—
5	EX.3*	—	—	—	—	—	—	—	—	—	—	—	0·32	—
6	EX.4*	—	—	—	—	—	—	—	—	—	—	—	0·62	—
7	EX.5*	—	—	0·86	—	—	—	—	—	—	—	—	—	—
8	EX.6*	—	—	1·60	—	—	—	—	—	—	—	—	—	—
9	JKL.1†	4·6	0·56	0·04	0·60	0·20	0·38	0·64	0·02	—	0·05	—	—	—
10	JKL.2†	4·6	0·56	0·04	0·60	0·20	0·29	0·64	0·02	—	0·05	—	—	—
11	JKL.3†	4·54	0·49	0·03	0·61	0·69	—	0·64	0·02	—	—	0·48	—	—
12	JKL.4†	4·54	0·49	0·03	0·61	0·69	—	0·64	0·02	—	—	0·72	—	—
13	DFL.3	4·12	0·50	0·02	0·56	0·40	0·02	0·44	—	—	—	—	—	—
14	C.AWN	4·44	0·05	—	0·62	0·52	—	0·85	0·05	—	—	—	—	—
15	DRQ	3·04	0·53	0·05	0·005	0·24	0·14	0·42	—	—	0·54	—	—	—
16	JPV	4·22	1·50	—	—	0·24	—	0·78	1·90	—	—	—	—	—
17	DTF	0·02	3·07	0·03	0·51	0·24	—	—	—	—	—	—	—	—
18	W.AAA	1·88	2·36	6·92	0·13	0·15	—	0·22	—	—	—	—	—	—
19	TQK	1·86	1·01	—	0·05	0·84	—	0·89	1·05	0·09	—	—	—	—
20	C.AYO	3·11	0·80	—	0·42	0·26	—	0·46	—	—	—	0·19	0·13	—
21	NDA	—	0·88	tr.	0·34	0·14	—	0·51	—	0·11	—	—	—	0·52
22	NDB	—	<0·01	13·6	0·15	0·10	—	0·38	—	0·03	—	—	—	0·26
23	TAS	—	12·5	—	—	0·06	0·28	0·19	—	—	—	—	—	—
24	TAR	—	4·0	—	—	0·08	0·23	0·11	—	—	—	—	—	—
25	RPX	3·10	0·50	—	—	0·20	0·20	0·50	—	—	0·50	—	—	—
26	TBF	7·25	—	3·10	0·30	2·20	0·44	1·00	0·24	<0·05	0·06	—	0·14	—
27	TAK	2·98	0·11	tr.	0·29	5·58	0·08	0·68	0·10	—	0·10	—	—	—
28	L.I.	0·005	0·004	0·02	0·007	0·10	—	0·12	—	—	—	—	—	—
29	L.2	0·060	0·036	0·04	0·042	0·16	—	0·21	—	—	—	—	—	—
30	L.3	0·15	0·11	0·09	0·09	0·30	—	0·43	—	—	—	—	—	—
31	321	0·83	0·23	—	—	2·55	—	1·36	0·52	0·21	—	—	—	—
32	322	1·54	0·09	—	—	1·98	—	1·10	1·07	0·14	—	—	—	—
33	323	2·02	0·06	—	—	1·26	—	0·82	1·71	0·05	—	—	—	—
34	HA.1	3·75	0·42	—	0·37	0·34	—	0·35	—	0·009	—	—	—	—
35	HA.2	4·01	0·51	—	0·54	0·38	—	0·30	—	0·008	—	—	—	—
36	HA.3	4·41	0·71	—	0·67	0·43	—	0·32	—	0·008	—	—	—	—
37	HA.4	1·71	0·61	—	—	0·38	—	0·78	0·51	0·075	—	—	—	—
38	HA.5	2·04	0·92	—	—	0·61	—	1·03	0·91	0·089	—	—	—	—
39	HA.6	2·05	1·24	—	—	0·89	—	1·43	1·40	0·22	—	—	—	—
40	HA.7	0·005	—	—	0·005	9·96	—	0·32	—	0·014	—	—	0·0016	—
41	HA.8	0·006	—	—	0·009	11·82	—	0·33	—	0·011	—	—	0·0012	—
42	HA.9	0·007	—	—	0·014	13·17	—	0·37	—	0·011	—	—	0·0016	—
43	L.5	3·0	—	10·0	—	—	—	—	—	—	—	—	—	—

* Samples 2 to 8 inclusive were prepared by one of the authors from pure metals; then analysed.
† Samples 9 to 12 inclusive were duralumin-type alloys to which tin, antimony and bismuth were added.

PART II

MAGNESIUM-BASE ALLOYS

Magnesium does not offer a very wide range of either alloys or alloying elements, the three main additions being aluminium, manganese and zinc. Of the other alloying elements that might be used only copper, antimony and cadmium seem worth while from the point of view of spot-testing. The highly reactive nature of magnesium has made the evolution of suitable tests more difficult than any hitherto attempted. Tests have, however, been evolved for the following elements: aluminium, manganese, zinc, copper, antimony, and cadmium.

(I) ALUMINIUM

Reagents—(*a*) Mixture of acetic acid solution (10%), 1 vol.; sodium sulphide solution (10%), 1 vol.
(*b*) Oxalic acid solution (10%).
(*c*) Potassium cobalticyanide solution (10%).
(*d*) Alizarin "S" solution (0·25% in water).

Method—Place 2 drops of (*a*) on the thoroughly cleaned surface and leave to react for 3 minutes. Add 2 drops of (*b*) followed by 2 drops of (*c*) and stir well. Add 3 drops of (*d*) and again stir thoroughly. In presence of aluminium, the drop, which has originally a yellowish-golden colour, slowly develops an orange-coloured precipitate; with samples of low aluminium content it may be 3–4 minutes before the precipitate is formed. After 4–5 minutes the drop, and precipitate if any, is transferred, by means of a capillary tube, to the centre of a disc of No. 41, 12·5 cm. filter paper, supported on the open mouth of a beaker, the solution being added dropwise and each drop being allowed to spread before the next is added. The spot is washed twice with 2–3 drops of distilled water, dropped in the centre of the paper and allowed to spread.

During the 4–5 minutes the reagents are on the sample, a reddish magenta colour slowly forms around the edge of the drop; this is mainly due to magnesium and does not affect the test, since the colour disappears if the drop is stirred immediately before it is removed from the sample.

In absence of aluminium the general colour of the paper is yellow or, for certain elements, magenta; all papers dry to varying shades of magenta. When dry, the aluminium precipitate is seen as an orange-red spot against a background of varying shades of magenta.

Tried on: Samples Nos. **61, 50, 53, 49, 54, 45, 55, 48**—Aluminium present; all gave positive results.
Nos. **47, 44, 62, 56, 58, 59, 67, 72**—Aluminium absent and all results negative.

(II) Manganese

Reagents—(*a*) Nitric acid (sp.gr. 1·20) containing 2·5% of potassium bromate.
(*b*) Nitric acid (sp.gr. 1·20).
(*c*) Sodium bismuthate (solid).

Method—Place 3 drops of (*a*) on the thoroughly cleaned sample and leave until the reaction appears to be complete. To the well of a white porcelain spot-plate add 3 drops of (*b*) and to this add the reaction solution, transferred by means of a capillary tube; stir well. Add a small quantity of (*c*) from the point of a pen-knife blade, stir and leave for 5 min. In presence of manganese, say, over 2 per cent., a very intense purple coloration of permanganic acid is produced; 0·4–0·6 per cent. gives a fair to strong reaction; 0·1 per cent. gives a faint purple colour. (The test cannot be carried out on the sample, since bismuth metal is deposited on the magnesium.) In absence of manganese the drop remains water-white in colour.

Tried on: Samples Nos. **56, 62, 51, 55, 53, 54, 49, 50, 52**—Manganese present; all results positive.
Nos. **44, 45, 48, 58, 61, 47, 59, 61, 67, 72**—Manganese absent; all results negative.

(III) Zinc

Reagents—(*a*) Ammonium nitrate solution (20%).
(*b*) Distilled water.
(*c*) Diphenylcarbazone (saturated solution in amyl alcohol).
(*d*) Mixture of diluted acetic acid (1 in 50), 1 vol.; ammonium acetate solution,* 1 vol.

Method—To the thoroughly cleaned surface add 3 drops of (*a*) and leave to react for at least 5 minutes. Wash off the drop with 4 drops of (*b*) on to a clean watch glass. Add to the transferred drop 2–3 drops of (*c*) followed by 5 drops of (*d*); stir well. In presence of zinc, manganese or cadmium a magenta-blood-red colour is produced; on stirring well, the colours due to manganese and cadmium are bleached to a brownish red (colour of the reagent) whilst the cherry-red colour due to zinc remains stable. In absence of the above-mentioned metals the initial colour of the drop after the addition of reagent (*c*) is a brownish red. The

* Preparation of ammonium acetate solution: add, to 1140 ml. of distilled water in a 3-litre porcelain beaker placed in a cooling bath, 500 ml. of 0·880 ammonia solution followed by 570 ml. of glacial acetic acid, the solution being stirred continuously. Allow to cool; the solution should be neutral.

colours of the above reactions occur in the amyl alcohol layer and are stable so long as any amyl alcohol remains.

Tried on: Samples Nos. 67, 52, 68, 69, 70, 66, 72, 71—Zinc present; all gave positive results.
Nos. 44, 56, 59, 51, 58, 47, 49, 50, 45—Zinc below 0·06 per cent. and all results negative.

(IV) Copper

Reagents—(*a*) Nitric acid (sp.gr. 1·20).
(*b*) Mixture of α-benzoin-monoxime in alcohol (saturated solution), 10 vols.; diluted ammonia (1+1), 20 vols.; citric acid solution (50%), 5 vols.
(*c*) Ammonium persulphate (solid).

Method—Place 2 drops of (*a*) on the thoroughly cleaned sample and leave until the reaction appears complete. Wash off the drop with water and dry the specimen with an acetone wash. Add 3–4 drops of (*b*) followed by a few crystals of (*c*), mix in the crystals and leave for about 5 minutes. In presence of copper a dirty green precipitate will slowly be developed. In absence of copper a white deposit will be observed due to the precipitation of α-benzoin-monoxime as the alcohol evaporates. The only two samples containing copper available were Nos. 45 and 48; both samples, each containing 5 per cent. of copper, gave a strong reaction.

Tried on: Samples Nos. 45, 48—Copper present; both gave positive results.
Nos. 44, 47, 49, 52, 56, 58—Copper absent and all results negative.

(V) Antimony

Reagents—(*a*) Mixture of tartaric acid solution (50%), 1 vol.; bromine water (saturated solution), 1 vol.
(*b*) Diluted hydrochloric acid (1 in 10).
(*c*) Sodium hypophosphite (solid).
(*d*) Copper foil (approx. 3/16 inch square).

Method—Place 6 drops of (*a*) on the thoroughly cleaned surface and allow to react until the bromine colour has nearly disappeared; then quickly wash the drop into a 60 ml. tall-form beaker, with a few drops of water. Add 10 ml. of (*b*) followed by about 0·5 g. of (*c*) and the piece of copper foil (*d*) (previously cleaned with nitric acid) taking care not to touch the copper foil with the fingers. Boil the solution gently until the salts begin to crystallise and the volume of liquid left is about 1–2 ml.; cool and dilute with water. Place the beaker on a white glazed tile for comparison with a blank test run under exactly the same conditions; comparison should be made by looking vertically downwards on to the beakers. Even small amounts of antimony give a purple tint to the copper foil. In absence of antimony the copper remains bright. A sample containing 10 per cent. of bismuth gave a slight grey deposit, but this was less than the deposit from 0·16 per cent. of antimony which, in any case, is purple.

Tried on: Samples Nos. 47, 49, 46—Antimony present; all gave positive results.
Nos. 44, 50, 51, 52, 56, 59, 61, 62, 67, 72—Antimony absent and all results negative.

(VI) Cadmium

Reagents—(*a*) Diluted sulphuric acid (1+3).
(*b*) Mixture* of diluted ammonia (1+1), 3 vols; potassium cyanide solution (10%), 1 vol.
(*c*) Mixture* of sodium sulphide solution (10%), 1 vol.; potassium cyanide solution (10%), 3 vols.; ammonium nitrate solution (20%), 4 vols.
(*d*) Diluted acetic acid (1 in 20).

Method—To the thoroughly cleaned surface of the sample add 3 drops of (*a*) and leave to react until the vigorous attack has subsided; this usually takes about 1 min. Wash off the drop with a jet of distilled water on to a clean watch glass. Add 4 drops of (*b*), which

* These solutions lose their strength quickly if left open to the atmosphere, they should be made up fresh before use and kept covered during the testing of samples.

should make the resulting solution ammoniacal; stir and then add 4 drops of (*c*), stir again and leave for 10 minutes. Remove the solution from the watch-glass by means of a capillary tube, filter through a glass-tube filter-pulp,* as for "Vanadium in Steel,"[1] and wash with 2 drops of (*d*). In presence of cadmium a yellow precipitate will be observed in the solution,

TABLE II—MAGNESIUM ALLOYS

Percentages

No.	Mark	Al	Mn	Sb	Cu	Zn	Cd	Si	Fe
44	Pure Mg	—	—	—	—	—	—	—	—
45	Cu A.3	5·0	—	—	5·0	—	—	—	—
46	SB.2	—	—	0·16	—	—	—	—	—
47	SB.4	—	—	2·0	—	—	—	—	—
48	Cu A.2	1·0	—	—	5·0	—	—	—	—
49	TAD	8·25	0·29	0·26	—	—	—	—	0·01
50	SZY	9·40	0·21	—	0·03	0·05	—	0·06	0·02
51	SCP	<0·01	1·9	—	—	tr.	—	tr.	0·03
52	SCQ	0·30	0·10	—	—	3·3	2·1	tr.	0·05
53	2292	9·2	0·50	—	—	—	—	—	—
54	2283	5·8	0·40	—	—	—	—	—	—
55	2277	3·8	0·60	—	—	—	—	—	—
56	503	—	2·0	—	—	—	—	—	—
57	S.768	—	—	—	—	—	0·76	—	—
58	EX.43	—	—	—	—	—	2·06	0·70	—
59	S.765	—	—	—	—	—	1·46	<0·05	—
60	S.766	—	—	—	—	—	0·97	<0·05	—
61	AL.3	10·0	—	—	—	—	—	—	—
62	MN.1	—	2·0	—	—	—	—	—	—
63	S.769	—	—	—	—	—	0·40	—	—
64	S.770	—	—	—	—	—	0·25	—	—
65	S.771	—	—	—	—	—	0·23	—	—
66	S.772	—	—	—	—	2·84	0·95	—	—
67	S.773	—	—	—	—	3·64	2·19	—	—
68	S.774	—	—	—	—	3·34	0·78	—	—
69	S.775	—	—	—	—	3·24	0·23	—	—
70	S.776	—	—	—	—	2·85	0·16	—	—
71	S.777	—	—	—	—	0·67	—	—	—
72	S.778	—	—	—	—	2·25	—	—	—

if the cadmium content is high, and as a bright yellow film on the pulp in the filter-tube; black insoluble particles from the initial attack may tend to darken the yellow sulphide colour. Manganese gives a whitish precipitate on the watch-glass and a flesh-coloured film on the pulp; this precipitate of manganese sulphide however is completely dissolved in the 2 drops of (*d*) added. Aluminium is precipitated as the hydroxide but this does not destroy the effectiveness of the test. Zinc does not give a sulphide precipitate under these conditions.[3]

The yellow sulphide colour is roughly proportional to the cadmium content; down to about 0·16 per cent. was observed, this amount giving a pale yellow film on the pulp.

Confirmatory Test for Cadmium—

Reagents—(*e*) Ammonium nitrate solution (20%).
(*f*) Bromine water (saturated solution).
(*g*) Diluted ammonia (1+1).
(*h*) Diphenylcarbazone solution (1·5% in alcohol).

Method—Having filtered off the cadmium sulphide, which is retained on the pulp of the glass filter tube, continue as follows:—Remove the tube to a fresh spot of the filter pulp and wash three times with 3 drops of (*e*), allowing each wash to soak through completely before the addition of subsequent drops. Remove the filter tube to the centre of a disc of 12·5 cm. No. 541 filter paper supported on the open mouth of a beaker. Add 1 drop of (*f*) followed by three single-drop washings with distilled water. Remove the glass filter tube, place the disc of filter paper over (*g*) contained in a 4·5 inch Petri dish and leave, covered, for 1 minute for any free acid to be completely neutralised. Replace the filter paper on the mouth of the

* The glass-tube filter-pulp was placed on a large filter pulp contained in a funnel, this saves the use of filter discs and has the advantage that several filter tubes can be operated at once in a comparatively small space.

beaker and leave for 2–3 minutes for the excess ammonia to evaporate. Add 4 drops of (*h*) to the centre of the wet patch, allow to spread, then add a further 4 drops of (*h*) and again allow to spread; carefully observe the reactions that take place. In presence of large amounts of cadmium the reagent spreads outwards with an outer violet-purple band, which becomes blackish-purple within 1 minute of the first addition of reagent (*h*). This band, which assumes the form of an irregular ring, always lies just inside the outer edge of the reagent patch; the remainder of the area inside the ring is of a magenta colour. With low cadmium contents the appearance of the violet-purple band and the separation of the blackish purple irregular ring is a trifle delayed but is well developed within 1 minute of the first addition of reagent (*h*). In absence of cadmium, the colour of the reagent patch is red to reddish brown, probably owing to a little ammonia still left in the pores of the paper; the colour considerably lightens as drying proceeds; there is no blackish purple ring after 1 minute but in its place is a light brown ring.

Tried on: Samples Nos. 67, 52, 58, 59, 60, 66, 68, 57, 63, 64, 65, 69, 70—Cadmium present; all gave positive results.
Nos. 51, 72, 56, 47, 53—Cadmium absent and all results negative.

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The Rapid Determination of Small Quantities of Nickel with Dithizone

BY R. S. YOUNG, E. H. STRICKLAND AND A. LEIBOWITZ

THE dimethylglyoxime procedure for nickel is one of the most satisfactory methods in the entire field of analytical chemistry. Nevertheless there are occasions when rapid determinations of very low concentrations of nickel are required, for which the standard dimethylglyoxime procedure is unsuitable owing to the necessity for large volumes and the long time needed for the formation of a precipitate. An important instance of this is the determination of nickel in zinc solutions in electrolytic zinc refineries. Since nickel is one of the most deleterious impurities in the cell room, the nickel purification step calls for careful control and the determination of very small quantities of this metal. The quantities of nickel tolerated generally range from 0·1 to 0·4 mg. of nickel per litre, and since the solutions are in process the results are required in a hurry. The following method, while developed primarily for this purpose, has been used for other metallurgical products and is believed to have wide application to other industries where a rapid determination of small quantities of nickel is required.

Various procedures for the determination of traces of nickel have been recently reviewed in Sandell's excellent monograph.[1] With the exception of further work reported on colour comparisons with the red colour given by oxidised nickel with dimethylglyoxime,[2,3] and a method using the colour of nickel dimethylglyoxime in pyridine,[4] no later papers on this subject have come to the authors' notice. Although it has been known for some years that nickel was one of the dozen metals that react quantitatively with dithizone, there are very few references in the literature on this reaction, compared with the volume of work reported with lead, mercury, zinc and other metals. In view of the sensitivity of nickel towards dithizone, and its relative ease of manipulation for plant control, a titrimetric method was used for this work.

METHOD

PRINCIPLE—

Nickel, like zinc, lead, cobalt, cadmium and several other elements, reacts with dithizone only in alkaline solution. Since a number of metals, such as copper, react with dithizone both in acid and in alkaline solution, the rapid determination of nickel in a complex sample with dithizone depends on its prior isolation with dimethylglyoxime and extraction of the resulting nickel glyoxime with chloroform. When the chloroform extract is shaken with

dilute acid the nickel is transferred to the aqueous layer, and can then be determined by the usual titrimetric procedure with dithizone. Apart from palladium, practically no element apt to be encountered in practice will interfere.

REAGENTS—

Dimethylglyoxime solution—Dissolve 1 g. of dimethylglyoxime in 100 ml. of ethyl alcohol.

Dithizone solution—Dissolve 0·25 g. of diphenylthiocarbazone in 1 litre of carbon tetrachloride to give a stock solution of which 1 ml. ≡ approximately 0·01 mg. of nickel. It must be standardised frequently against a nickel solution of known concentration and should be kept in a large separating funnel covered with a dark cloth and having a layer of sulphurous acid over the solution. An assembly of this large separating funnel and the 10 ml. burette on one Fisher burette holder makes a very convenient arrangement. Weaker dithizone solutions can be made by dilution with carbon tetrachloride.

Nickel solution—A solution containing 0·0448 g. of AnalaR $NiSO_4.6H_2O$ per litre contains 0·01 mg. of Ni per ml.

Sodium acetate - ammonium thiocyanate solution—Mix 3 parts by volume of saturated sodium acetate solution with 1 part of saturated ammonium thiocyanate solution.

Sodium citrate solution—Dissolve 25 g. of sodium citrate in 50 ml. of water and transfer to a dropping bottle.

PROCEDURE—

If the nickel is not in solution, dissolve it by appropriate acid treatment. Nearly all metallurgical materials can be rapidly decomposed by treatment with nitric acid after addition of potassium chlorate. Boil thoroughly to remove all oxides of nitrogen and free chlorine. It is generally unnecessary to add other acids or to evaporate to dryness. Dilute with water, filter if necessary, and wash thoroughly.

Transfer to a volumetric flask and make up to volume. Pipette a 2–25 ml. aliquot containing 0·01–0·1 mg. of nickel to a 60 or 75 ml. separating funnel. Add sufficient 50 per cent. sodium citrate or tartrate solution, usually 5 drops, to hold the iron in solution, and 1–2 ml. of dimethylglyoxime solution. Add ammonia until the solution is faintly alkaline, shaking to ensure thorough mixing. This point can be readily observed by addition of a drop or two of B.D.H. universal indicator, which gives a blue colour at *p*H 8. In presence of large quantities of cobalt, manganese or zinc, the precipitation of nickel is improved by the presence of ammonium acetate in the ammoniacal solution.

Add 12 ml. of chloroform and shake the separating funnel vigorously for half a minute to extract all the nickel. When the chloroform layer settles to the bottom transfer it to another separating funnel, or draw off the upper, nickel-free aqueous layer by means of a fine glass tube attached to a suction bottle, and discard.

Remove traces of copper and other metals from the chloroform layer by shaking several times with 2 per cent. ammonium hydroxide solution to which has been added a few drops of dimethylglyoxime, and drawing off the upper layer with a suction bottle. The lower layer contains the nickel

Transfer the nickel from the chloroform layer to an aqueous layer ready for titration with dithizone by shaking vigorously with 12 ml. of 2 per cent. hydrochloric acid. Draw off and discard the lower layer of chloroform. A drop of B.D.H. universal indicator facilitates the separation of these colourless layers.

Remove traces of dimethylglyoxime from the weakly acid nickel solution by shaking twice with 5 ml. portions of ether, withdrawing the ether each time by the suction bottle. A drop of universal indicator here also aids the detection and separation of the upper, ether layer from the aqueous portion.

Add 4 ml. of saturated sodium acetate - ammonium thiocyanate solution, a drop of universal indicator, and ammonia until *p*H 8 is reached. To the separating funnel add a small quantity of standard dithizone solution from a 10 ml. burette and shake vigorously until the lower green dithizone layer turns purple. This shows that all the dithizone has reacted with nickel to form the purple nickel dithizonate. Draw the latter off, add more dithizone, shake, and continue in this manner until finally the green dithizone solution remains green after vigorous shaking, indicating that all the nickel has been extracted. The number of ml. of standard dithizone solution which have turned from green to purple is a measure of the quantity of nickel present. The dithizone is standardised in the same way against a nickel salt carried through all the steps of the procedure. A blank determination must be

made, since even with scrupulous care and exclusive use of Pyrex glassware, traces of other metals that react with dithizone in alkaline solution will result in a small blank.

The interesting observation was made that the green dithizone solutions, which appear red when viewed against ordinary electric lighting, have the brilliant green colour when the source of the transmitted light is one of the daylight fluorescent tubes now coming into wide use for laboratory and industrial lighting. This has obvious applications for all dithizone determinations carried out at night or in poorly-lighted locations.

Practically no other common element interferes with the determination as outlined above. If large quantities of bismuth are present it will be necessary to have sufficient tartrate present prior to the addition of dimethylglyoxime to prevent formation of the bismuth complex with the latter. Palladium will interfere, but in the rare instances where it might be encountered a prior separation with dimethylglyoxime in acid solution would remove palladium together with any co-precipitated platinum and gold from the nickel solution. In any case platinum in the fully oxidised form does not react with dithizone, and practically all the gold is removed with the ether rinsings of the dilute hydrochloric acid solution.

APPLICATIONS—

The procedure described is suitable for the rapid determination of very small quantities of nickel in a wide variety of materials. It avoids the use of large samples and the long period of standing—8–48 hours—necessary with dimethylglyoxime for the formation and precipitation of very small quantities of nickel. When dealing with solutions alone, the use of an analytical balance, hot plates, and a complete laboratory is unnecessary, and the determination can be carried out in the plant by any skilled operator, with occasional checking of the dithizone standards, etc., by the laboratory.

EXAMPLES OF RESULTS—

Some examples of results obtained with this procedure are illustrated in Table I. The values obtained for low concentrations of nickel with the standard gravimetric procedure using dimethylglyoxime were secured by careful analyses of very large samples.

TABLE I

	Nickel, determined by	
	Dithizone titrimetric procedure	Dimethylglyoxime gravimetric procedure
Zinc tank house solution A, mg./litre	0·09	0·1
,, ,, ,, ,, B, mg./litre	0·41	0·4
Copper tank house stripper solution, g./litre ..	2·81	2·87
,, ,, ,, heater solution, g./litre ..	7·35	7·29
,, ore, %	0·0007	0·0007
Cobalt ore, %	0·0001	0·0001
Blister copper, %	0·027	0·0265
Refined copper, %	0·0005	0·0005
Bureau of Standards No. 61 ferrovanadium, %	1·36	1·33

For samples containing considerable quantities of nickel, such as the Bureau of Standards ferrovanadium, the use of a necessarily small aliquot introduces an appreciable error inherent in all cases where a large factor must be used. Even here, however, the agreement with the rapid dithizone procedure employed is remarkably close.

SUMMARY—

A rapid procedure is described for the determination of very small quantities of nickel, which is applicable to a wide variety of materials. It is based on the isolation of nickel with dimethyglyoxime, its extraction with chloroform, transference to a dilute acid solution, and final titration in alkaline solution with a standard solution of dithizone. Practically no other element interferes, and the procedure is equally adapted for rapid plant control or accurate laboratory analyses.

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The Determination of Lead in Copper, Nickel and Cobalt by Dithizone

By R. S. YOUNG and A. LEIBOWITZ

Lead is an important impurity in copper. In British Standard Specifications for cathode, electrolytic, and fire refined high conductivity copper, only two impurities are specifically mentioned: bismuth and lead. The latter must not exceed 0·005 per cent. for the above classifications, whereas copper not intended for electrical purposes may contain 0·01, 0·02 or even 0·10 per cent. of lead in different grades.

In general, the amount of lead in blister copper may vary from 0·0001 to 0·4 per cent., and in refined copper from less than 0·0001 to over 0·005 per cent. The determination of these small quantities necessitates the use of a very large initial sample when lead is isolated and weighed as sulphate or chromate by conventional gravimetric procedures.

Yao[1] has recently described a dithizone method for the determination of bismuth in copper. A similar procedure, with appropriate modifications and extensions, may be employed for lead. The determination of small quantities of lead in biological and other materials by means of dithizone has been the subject of many investigations and a number of references, the latter being summarised recently in References 2, 3, 4, 5. The following procedure, while developed primarily for lead in copper, has been found equally valuable for the determination of this element in metallic nickel and cobalt.

Method

Dissolve in diluted nitric acid (1+1) a quantity of the copper sample sufficient to yield 0·02–0·05 mg. of lead. Owing to the segregation of impurities in copper and other metal samples, take a minimum weight of 10 g. in any case, and for the higher ranges of lead content dilute to a suitable volume and take an aliquot.

To the copper nitrate solution add about 30–50 times as much iron in the form of ferric nitrate solution as there is lead present. If the copper is very impure the quantity of iron added should be increased so that it approximates to 30 times the combined quantities of arsenic, antimony, bismuth, selenium, tellurium and lead present. For most coppers the addition of 5 ml. of 5 per cent. ferric nitrate solution will collect completely 0·05 mg. of lead plus any accompanying elements occluded by ferric hydroxide in this procedure.

Cautiously make ammoniacal and add 10 ml. excess. Heat just to boiling on the hot plate, remove, and filter through a Whatman 541 or similar paper. Wash several times with hot 10 per cent. ammonium hydroxide solution and hot water. Transfer the precipitate to the original beaker, dissolve in nitric acid, and re-precipitate with ammonia. Filter through the same paper, washing thoroughly with hot 10 per cent. ammonium hydroxide solution and finally with hot water.

Dissolve the precipitate of ferric hydroxide and occluded lead, etc., off the paper with a minimum quantity of hot diluted hydrochloric acid (1+1) and wash thoroughly with hot water. Adjust the concentration of hydrochloric acid present to a ratio of approximately 526 ml. of the concentrated acid to 474 ml. of water and remove the iron by an ether extraction. A small quantity of iron left in the lower layer after two extractions may be disregarded. Transfer the aqueous solution to a beaker and place on asbestos on the edge of a hot plate to evaporate the ether.

Cool and pour into a 100–250 ml. separating funnel. Add 1 ml. of 50 per cent. citric acid solution, several drops of B.T.L. universal indicator, and 10 per cent. ammonium hydroxide solution until the appearance of the green colour denoting *p*H 8. Then add 4–5 ml. of 50 per cent. potassium cyanide solution.

Add the standard dithizone from a burette in 5-ml. portions at a time and shake the separating funnel vigorously. Draw off and retain the orange-red dithizonates of bismuth and lead each time in another small separating funnel. When the lower carbon tetrachloride layer in the first funnel remains green after being shaken vigorously for a minute it can be assumed that all the bismuth and lead have been extracted. Excess of dithizone is not harmful, and it is unnecessary to record the volume of dithizone used in this preliminary extraction. Thallous thallium and stannous tin are also extracted by dithizone from alkaline cyanide solution, but the prior decomposition in nitric acid will have eliminated this interference.

To the extracted dithizonates add 10 ml. of 4 per cent. potassium cyanide solution and

shake well to remove traces of other metals into the upper aqueous layer. Withdraw the lower red or orange dithizonate layer into another separating funnel and rinse this portion in the same way with 4 per cent. potassium cyanide solution. To the final washed solution of dithizonates add 10 ml. of 5 per cent. nitric acid and shake vigorously to transfer lead and bismuth to the dilute acid phase. Draw off and discard the lower green layer.

Add several drops of *m*-cresol purple indicator, adjust the *p*H with dilute ammonium hydroxide solution to approximately 2, add 2 ml. of 10 per cent. hydroxylamine hydrochloride solution, and adjust the *p*H carefully to *p*H 2–3.

Extract the bismuth by successive additions of standard dithizone solution from a 10-ml. burette, shaking the funnel vigorously for one minute and withdrawing the orange dithizonate each time. When the lower carbon tetrachloride layer remains green all the bismuth has been removed. If a quantitative measure of the bismuth is desired the volume of dithizone used multiplied by the bismuth value of this solution will give the quantity of bismuth present. The dithizone solution may be standardised daily against a standard solution of bismuth in dilute nitric acid, containing 0·01 mg. of bismuth per ml.

Now add 1 ml. of saturated sodium acetate solution, 2 ml. of 50 per cent. potassium cyanide solution, several drops of B.T.L. universal indicator, and 2 ml. of 10 per cent. hydroxylamine hydrochloride solution, and adjust the *p*H of the solution to 8 with dilute ammonium hydroxide solution and dilute nitric acid. Add successive small portions of standard dithizone solution from a burette, shaking vigorously for one minute, and withdrawing the red lead dithizonate each time, until the carbon tetrachloride phase remains green, indicating complete extraction of lead.

If the sample does not contain bismuth, of course, the procedure can be shortened by extracting at *p*H 8, after isolating the lead with potassium cyanide solution and rinsing twice with 10 ml. of 4 per cent. potassium cyanide solution. Very few coppers, however, fail to contain traces of bismuth, and it is nearly invariably necessary to remove bismuth in acid solution first. In this way bismuth and lead may be determined by dithizone on the same sample.

Standardise the dithizone solution against a standard lead nitrate solution containing 0·0160 g. of AnalaR $Pb(NO_3)_2$ per litre. One ml. of this solution contains 0·01 mg. of lead. The standard dithizone solution may contain 0·025 g. of diphenylthiocarbazone in 1 litre of carbon tetrachloride. One ml. of this dithizone solution should correspond approximately with 0·01 mg. of lead.

Lead, and bismuth if necessary, can be determined in the same manner in metallic nickel and cobalt, or in solutions of their salts. In this case a large excess of ammonia is desirable when precipitating and filtering off ferric hydroxide, in order to minimise adsorption or occlusion of nickel and particularly of cobalt.

As in all work with dithizone, scrupulous care is necessary to avoid contamination in reagents or glassware. Careful blanks should be run regularly, and occasionally the results can be checked against the laborious gravimetric procedure where a 500-gram or similar large sample is employed. Lead can be removed from reagents by shaking with dithizone at *p*H 7–9 until metal dithizonates are no longer present, and then removing any excess dithizone by shaking with carbon tetrachloride.

RESULTS—

The following results for lead in copper and other metals were obtained on known and unknown samples. In some instances the results by the dithizone procedure were carefully

TABLE I

DETERMINATION OF LEAD IN COPPER AND OTHER METALS BY DITHIZONE

Sample	Wt. aliquot sample g.	Lead added mg.	Lead found by dithizone %	Lead found by dithizone mg.	Lead found gravimetrically %	Lead found gravimetrically mg.
Blister copper ..	10	nil	0·00043	0·043	0·0004	0·04
	0·1	,,	0·052	0·052	0·051	0·05
Refined copper ..	50	,,	0·0001	0·052	0·0001	0·05
	1	,,	0·0046	0·046	0·0048	0·048
Nickel	5	,,	0·00066	0·033	0·0006	0·03
	5	0·05		0·074		0·08
Cobalt	25	nil	0·00014	0·072	0·00015	0·075
	25	0·05		0·088		0·0875

checked gravimetrically, using very large samples; in other instances the recovery of added lead was used as an indication of the accuracy of the method.

SUMMARY—

The determination of small quantities of lead in copper and other metals can be advantageously effected by a dithizone procedure Lead, together with arsenic, antimony, bismuth, etc., is collected by ferric hydroxide. Iron is removed by an ether extraction. Lead and bismuth are extracted by dithizone from an alkaline cyanide medium, and these metals are transferred to a dilute acid phase by shaking with nitric acid. Bismuth is then extracted at *p*H 2–3. Finally lead is titrated with dithizone in a solution buffered at *p*H 8.

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The Separation of Cobalt from Nickel and the Colorimetric Determination of Nickel

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IN a review of the literature on the colorimetric determination of nickel it was found that none of the methods so far described can be applied where the amount of cobalt present is greatly in excess of the nickel. When the nickel is determined directly on the solution of the sample after addition of bromine water or iodine and dimethylglyoxime,[1,2,3,4] the cobalt compound has been found in this laboratory to be formed preferentially to the nickel compound and the results are inaccurate. If the nickel compound is extracted by chloroform as in the method described by Sandell,[5] from a solution containing large amounts of cobalt, some of the cobalt compound will also be extracted. It was therefore found necessary to separate the cobalt from the nickel and a search was made in the literature to attempt to discover some rapid method for this separation. The gravimetric separation of nickel from cobalt by precipitation with dimethylglyoxime is a lengthy proceeding requiring at least two precipitations and long standing of the samples; it is not satisfactory for the precipitation of small amounts of nickel in samples containing large amounts of cobalt, iron, aluminium, magnesium, calcium, etc. Other methods for the separation of cobalt from nickel are available such as the well-known precipitation of cobalt with α-nitroso β-naphthol or with potassium nitrite. Cobalt may also be separated from nickel as the cobalticyanide,[6] as the xanthate,[7] as the phosphate,[8] or as the sulphide.[6] Most of these methods are somewhat protracted, and the precipitation methods are not suitable for the separation of large amounts of cobalt from very small amounts of nickel. In some cases the presence of excess reagent left in the nickel solution is objectionable in the colorimetric determination of nickel.

A method for the separation of cobalt from nickel has been developed in this laboratory in which cobalt is complexed with ammonium thiocyanate and extracted by means of a mixture of amyl alcohol and ether. Provided the amount of cobalt present is not too large (0·2 g. at the most) it may be extracted quickly and presence of excess of thiocyanate does not interfere with the nickel determination.

METHOD

REAGENTS—*Sodium phosphate solution*: Sixty-eight g. of tribasic sodium phosphate, $Na_3PO_4.12H_2O$, dissolved in 1 litre of water. *Ammonium thiocyanate solution*: 60 per cent. in water. *Amyl alcohol - ether mixture*: three parts of amyl alcohol to one part of ether, by volume *Ammonium citrate solution*: 500 g. of citric acid are dissolved in 500 ml. of ammonia and made up to 1 litre with water. *Ammoniacal dimethylglyoxime solution*: 1 g. of dimethylglyoxime is dissolved in 500 ml. of ammonia and made up to 1 litre with water. *Iodine solution*: *N*/10. *Chloroform*: C.P. *Ethyl alcohol*: absolute *Ethyl ether*. *Nitric acid*: one

part of nitric acid (sp.gr. 1·42) to one part of water. *Nickel sulphate solution*: 0·0957 g. of AnalaR $NiSO_4.7H_2O$ is dissolved and made up to a litre in water with addition of 10 ml. of sulphuric acid. This solution is standardised to contain 0·02 mg. of nickel per ml.

CALIBRATION GRAPHS—Measure 2, 3, 4, etc., up to 20 ml. of the standard nickel solution into separating funnels. Add to each 1 ml. of diluted nitric acid (1+1), 10 ml. of ammonium citrate solution and 20 ml. of ammoniacal dimethylglyoxime solution. Leave the solutions to stand for a minute or two to allow the colour to develop. Add 12 ml. of chloroform and shake well. Run off 6 ml. of the chloroform extract into a 10 ml. measuring cylinder, transfer to a small beaker and add 4 ml. of absolute alcohol. Mix the contents of the beaker well and pour into a 1 cm. absorptiometer cell. Compare the absorption of the chloroform extract with that of a water cell in the Spekker Absorptiometer, using spectrum violet filters. Plot the extinction values against mg. of nickel to obtain the calibration graph.

To check the results a second calibration graph may be constructed using the method described by Haywood and Wood.[4] To 1, 2, 3, etc., up to 10 ml. of the standardised nickel solution in 100 ml. graduated flasks add 5 ml. of $N/10$ iodine solution, 10 ml. of ammonium citrate solution and 20 ml. of ammoniacal dimethylglyoxime solution. Make the contents of each flask up to the mark with water and mix well. Pour the solutions into 1 cm. absorptiometer cells and compare with a water cell in the Spekker Absorptiometer, using spectrum blue filters. The same procedure is applied to a blank on the reagents, which will be found to give a small reading. Plot the extinction values against mg. of nickel. Diagrams of the calibration graphs have been omitted here in order to save space, and a graph constructed for one absorptiometer cannot be applied to readings taken on another instrument.

DETERMINATION OF THE NICKEL CONTENT OF SAMPLES—

Weigh out from 10 to 2 g. of the samples, according to the anticipated nickel content. A 10 g. sample covers the range 0·0002 to 0·004 per cent. of nickel and a 2 g. sample 0·001 to 0·02 per cent. For percentages of nickel in excess of these, smaller samples may be taken or aliquots of large samples. Decompose the samples with hydrochloric and nitric acids, and 10 ml. of diluted sulphuric acid (1+1). Add hydrofluoric acid and bromine if necessary. Evaporate the samples to fuming and dissolve in water.

Separation of the hydrogen sulphide group elements—If large amounts of copper are present this element may be removed by a preliminary electrolysis. Other elements of this group may be removed by gassing with hydrogen sulphide.

Separation of the iron—If large amounts of iron are present it is best to remove this element before the cobalt separation. In this laboratory a method for the separation of cobalt and nickel from iron is used in which sodium phosphate is first added to the solution and then ammonia until a *p*H of approximately 5·6 is attained. The *p*H is lowered by addition of 10 ml. of acetic acid and the ferric phosphate is precipitated on addition of an oxidising agent. For the colorimetric determination of nickel it was found that acetic acid appeared to interfere. In this case oxidise the sample solution with a few ml. of hydrogen peroxide solution and add 10 ml. of sodium phosphate solution for each 0·1 g. of iron present. Run in ammonia until it can be seen that the ferric phosphate is precipitating, but the solution must remain acid to litmus. Boil the samples and filter off the ferric phosphate precipitate through a No. 2 Whatman paper or by means of a Buchner funnel and suction using a No. 50 Whatman paper. Wash the precipitates well with hot water.

Alternatively the iron may be removed by extraction with ether. For this it is necessary to have the samples in hydrochloric acid solution, so sulphuric acid is omitted in the preliminary decomposition. Take the samples up in solution with three parts of concentrated hydrochloric acid to 1 part water and separate the iron by two extractions with ether. The samples must be subsequently evaporated to fuming with sulphuric acid before the removal of the hydrogen sulphide elements.

Separation of the cobalt—The samples must be reduced in bulk to approximately 100 ml. and oxidised with hydrogen peroxide. Transfer the samples to separating funnels. For samples containing 0·1 g. of cobalt add 50 ml. of ammonium thiocyanate solution, and for those containing 0·1 to 0·2 g. of cobalt add 75–100 ml. Add 20 ml. of the amyl alcohol - ether mixture and shake well. Run off the lower aqueous layer into another separating funnel and to it add a further 20 ml. of amyl alcohol - ether mixture. Repeat the extractions until the amyl alcohol - ether layer is colourless or faintly blue. If all the iron has not been removed the first two cobalt extracts will be purplish red in colour, but all subsequent extracts should be blue.

Determination of nickel—After extraction of the cobalt run the lower aqueous layer into a beaker and warm gently until the absorbed amyl alcohol and ether have been driven off. Cool, add 10 ml. of diluted nitric acid (1+1) and 10 ml. of ammonium citrate solution and run in ammonia until the solution is just alkaline to litmus. Cool again, transfer to separating funnels and add 20 ml. of ammoniacal dimethylglyoxime solution. Allow to stand for a minute or two and then add 12 ml. of chloroform. Shake well. Run off 6 ml. of the chloroform extract into a 10 ml. measuring cylinder, transfer to a small beaker, add 4 ml. of absolute alcohol and mix. Measure the absorption of the chloroform extract in the Spekker Absorptiometer, using 1 cm. cells and spectrum violet filters. The amount of nickel present in the sample is twice the amount read off from the calibration graph.

Checking the results—If there is any reason to suspect that all the cobalt has not been removed and that some cobalt compound may have been extracted along with the nickel, transfer the whole of the 10 ml. of final chloroform-plus-alcohol extract to a small beaker and add 2 ml. of diluted sulphuric acid (1+1). Heat gently until the chloroform has been expelled and cool the solution. Add 5 ml. of $N/10$ iodine solution, 10 ml. of ammonium citrate solution and 20 ml. ammoniacal dimethylglyoxime solution. Cool and transfer to a 100 ml. graduated flask. Make up to the mark with water and mix well. Measure the absorption, using 1 cm. absorption cells and spectrum blue filters. Read off the amount of nickel present from the second calibration graph. This should agree with the amount of nickel present as determined by measuring the absorption of the chloroform extract. If any cobalt has been extracted in the chloroform the second result will be lower than the first.

RESULTS—

The standard samples available in this laboratory on which nickel had been determined gravimetrically contained either no cobalt or only a very small amount. The nickel was therefore determined colorimetrically on these samples both before and after addition of standard cobalt solution.

RESULTS

Sample	Cobalt present %	Cobalt added g.	Nickel found	
			Gravimetric %	Absorptiometric %
Refined copper ..	0·0001	—	0·0005	0·0005
,, ,, ..	0·0001	0·1	—	0·0005
Blister ,, ..	0·0104	—	0·0265	0·027
,, ,, ..	0·0104	0·1	—	0·028
U.S.B.S. No. 61* ..	nil	—	1·33	1·35
,, ,, * ..	,,	0·1	—	1·35

* United States Bureau of Standards,

INTERFERING ELEMENTS—

Of the more common elements, those which are not removed in the original dissolution or in the separation of the hydrogen sulphide group are: aluminium, calcium, chromium, magnesium, manganese, phosphorus, titanium, uranium, vanadium, zinc, and zirconium. Of these, aluminium, chromium, magnesium, manganese, phosphorus, zinc, and zirconium do not interfere in any way with the determination of nickel, even when present in amounts of 0·2 g.

Calcium does not interfere with the determination of nickel but if the iron has been precipitated with sodium phosphate and an excess of phosphate solution has been added then the calcium will be precipitated as calcium phosphate after the final addition of ammonia. It is necessary in this case to allow the sample to stand for a short time and to filter the solution into the separating funnel. If the iron has been precipitated as the phosphate, titanium and uranium will have been completely removed. If this has not been done titanium and uranium will form yellow complexes with ammonium thiocyanate and will impart a green colour to the cobalt extracts. If these two elements are present in excess of cobalt the extractions must be continued until they are yellow in colour. If the amyl alcohol and ether are subsequently driven off, residual uranium and titanium will not interfere with the colorimetric determination of nickel. Vanadium when present in large amount will form a violet complex with ammonium thiocyanate and will be extracted with the cobalt. Vanadium does not interfere with the colorimetric determination of nickel but solutions containing vanadium which have been reduced by gassing with hydrogen sulphide should be oxidised with $N/10$ permanganate solution before the extraction of cobalt is attempted.

Discussion of the Method

The first calibration graph is not carried beyond 0·2 mg. of nickel. Beyond that point it is difficult to separate all the nickel by one extraction with chloroform and at 0·3 mg. of nickel the red nickel dimethylglyoxime compound commences to precipitate in the chloroform. The graph was found to cover the range of samples treated in this laboratory which contain large amounts of cobalt and are low in nickel. Twice the amount of nickel to be measured is always taken since it was found to be the most convenient way of carrying out the determination, as alcohol had always to be added to the chloroform in order to obtain an unclouded solution. The chloroform absorbs a small amount of water from the sample and from the glass vessels in which it is placed, and unless alcohol is added it is impossible to obtain a clear solution.

Sandell[4] found that although cobalt gave a coloured compound with dimethylglyoxime this did not enter the chloroform extract. He was working, however, with quantities in the neighbourhood of 5 mg. of cobalt and 5μg. of nickel, and it has been found by experiment in this laboratory that 5 mg. of cobalt is approximately the limiting value at which the cobalt compound will not enter the chloroform extract. With samples that contain cobalt in excess of 5 mg. the cobalt must always be separated. There is theoretically no limit to the amount of cobalt that may be extracted but if larger amounts than 0·2 mg. are present the number of extractions is considerably increased and so also is the amount of amyl alcohol - ether mixture consumed. The cobalt must be oxidised before extraction, otherwise it is very difficult to carry out a complete separation. Small amounts of iron may be extracted along with the cobalt as the ammonium thiocyanate compound, but if large amounts of iron are present in the samples it is better to separate the iron first. It was found that no nickel was held up in the ferric phosphate precipitate. Within reasonable limits the acidity of the sample solutions did not affect the determination of the nickel. In the analysis of the samples the solutions are neutralised with ammonia before the dimethylglyoxime is added. This is in order that the samples may be cooled and that no further heat may be developed before the chloroform is added, otherwise when shaking is commenced some of the chloroform and sample will be lost. However, this neutralisation may be dispensed with provided that the solution is left to become quite cool before the chloroform is added.

The dimethylglyoxime compound of nickel is formed rapidly after the addition of the reagent and its colour in the chloroform extract does not fade readily. Readings taken an hour after the extraction was made were the same as those taken immediately.

Conclusions—

(1) It was found that amounts of cobalt in excess of 5 mg. interfered with the colorimetric determination of nickel and a method is presented whereby cobalt may be separated from nickel more rapidly than by any method so far described.

(2) Nickel is determined colorimetrically by an adaptation of Sandell's method in which the intensity of colour of the chloroform extract is directly compared.

(3) The results may be checked by an application of Haywood and Wood's method.

(4) This colorimetric method cannot be claimed to be a rapid one but was worked out for special samples in which the amount of cobalt present greatly exceeds nickel. For such samples it may be carried through with greater speed than any method previously published.

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The Estimation of the Volatile Matter Content of Propellant Explosives

Part I.—The Estimation of Water by an improved Fischer Method

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An accurate knowledge of the moisture content of a propellant explosive is of considerable importance in assessing its influence on the ballistic properties of the propellant, particularly in relation to variations in moisture content with changes in temperature and humidity. In the few instances where determinations of the moisture content have been reported in the literature,[1,2] it is apparent that rather arbitrary methods have been employed which are unsatisfactory both for absolute estimations and for the measurement of small variations. It was evident that an accurate routine method was required for estimating quantities of water of the order of a few milligrams in all types of propellant explosives; for this purpose the procedure developed by Fischer[3] was investigated with a view to applying it to propellants.

The Fischer Reagent for the Estimation of Water—

The increasing employment of the Fischer reagent for the estimation of the water content of liquids and solids in recent years is an indication of the recognition of its wide applicability and high accuracy. The principle of this method of estimation was discovered by Fischer when attempting to determine the water present in liquid sulphur dioxide and mixtures of this with other solvents. He made use of the fact that sulphur dioxide is oxidised by iodine in presence of water and that decolorisation takes place owing to the disappearance of iodine in the reaction. The reaction was represented by the equation:

$$2H_2O + SO_2 + I_2 \rightleftharpoons H_2SO_4 + 2HI$$

The equilibrium was displaced completely to the right by addition of pyridine, which removed the acid products. For the estimation of water in organic solvents, Fischer employed the reagent now known by his name consisting of a solution of sulphur dioxide, iodine and pyridine in methyl alcohol. The reagent was standardised by titration with known amounts of water dissolved in methyl alcohol, the end point being detected by a change in colour from light yellow (due to the products of the titration) to brown when the whole of the water had reacted and excess of the reagent was present. As the reagent and the titration solution absorb atmospheric moisture very rapidly, Fischer employed the smallest possible vessels (100 ml. Erlenmeyer flasks) for the titrations to reduce the volume of air present. In a detailed study of the method by Smith, Bryant and Mitchell[4] they discovered that the reaction occurred in two distinct stages, and that one molecule of iodine reacted with only one molecule of water and not with two molecules as Fischer had assumed:

(1) $I_2 + SO_2 + 3C_5H_5N + H_2O = 2C_5H_5N.HI + C_5H_5N\langle^{SO_2}_{O}$

(2) $C_5H_5N\langle^{SO_2}_{O} + CH_3OH = C_5H_5N\langle^{SO_4CH_3}_{H}$

In applying the Fischer method these workers and others who followed usually employed methyl alcohol to extract the water from solids, transferring the methyl alcohol solution to a flask and either titrating directly with the Fischer reagent or adding an excess of the latter and titrating back with a standard solution of water in methyl alcohol. Although in general, steps were taken to exclude atmospheric moisture during the titration, the exposure of a large surface area of the hygroscopic methyl alcohol to the atmosphere at one or more stages of the determination was not avoidable. This factor assumes considerable importance when the quantity of water to be estimated is of the order of a few milligrams, but this has not always been emphasised by later workers. Other more obvious limitations were that the end-point colour change was insufficiently sensitive for the accurate determination of such small quantities of water, and coloured solutions, of course, were not titratable. The latter difficulties were overcome by Almy, Griffin and Wilcox,[5] who introduced a potentiometric method of detecting

the end-point, which depended on the change of potential of a platinum-tungsten electrode system immersed in the solution. A more sensitive method was reported by Wernimont and Hopkinson[6] by application of the dead-stop end-point technique used by Foulk and Bawden[7] in the detection of the end-point in iodimetric titrations. The dead-stop end-point technique depends on the fact that when a small electromotive force is applied to two platinum electrodes immersed in iodine solution a measurable current will flow while iodine is present to remove the hydrogen which tends to accumulate on the cathode, but immediately the whole of the iodine is removed (by titration) polarisation of the cathode by hydrogen accumulation occurs and a back e.m.f. is set up sufficient to overcome the small applied e.m.f., the current then ceasing to flow through the solution. A sensitive galvanometer included in this circuit registers the change of current and the attainment of the end-point is indicated by the return of the galvanometer needle to the zero of the scale. The technique was adapted to the Fischer method by adding a measured volume of the Fischer reagent in excess to the water solution to be estimated and titrating back the excess with a standard solution of water in methyl alcohol. A more refined technique for the dead stop end-point method was reported by McKinney and Hall[8] employing a "magic eye" electronic tube instrument in place of the sensitive galvanometer.

While studying the application of this modified Fischer method to the estimation of water in cordites and other solid explosives, which involved quantities of water of the order of a few milligrams, it became evident that it was of paramount importance to reduce to a minimum the possibility of interference by atmospheric moisture, and further a solvent less hygroscopic than methyl alcohol for the extraction of the water to be estimated was desirable. Two recent papers have provided details of methods for the estimation of very small quantities of water, in which specially designed apparatus is employed for the exclusion of atmospheric moisture during sampling and titration. Levy and others[9] claim to have estimated 1 to 25 mg. quantities of water with a precision of ± 20 to 100 μg., using a small titration vessel completely protected from the atmosphere by means of a tightly fitting rubber cap through which the samples and reagents are introduced by means of a hypodermic syringe. Aepli and Carter[10] report the estimation of 0–60 p.p.m. of water in liquid petroleum fractions, using an all-glass apparatus in which 150 ml. samples are transferred for titration to a 500 ml. four-necked flask fitted with a mercury-seal stirrer, exposure to the atmosphere being avoided during transfer. Both methods appear to be satisfactory for the special purposes for which they were devised, although it should be mentioned that in the first method a maximum error, *i.e.*, ± 100 μg. on 1 mg. is an error of ± 10 per cent., while in the second method the contents of the flask are transitorily exposed to the atmosphere at the stage immediately following the introduction of the 150 ml. sample.

The need for a simple inexpensive apparatus suitable both for general application and for the accurate estimation of a few milligrams of water is evident, and the apparatus and technique described below have fulfilled all requirements for such estimations in propellants and other explosives, and many other materials. The problem of providing a more suitable solvent than methyl alcohol for extraction of the water to be estimated was solved by use of diethylene dioxide (dioxan). Although pure dry dioxan is non-conducting under the conditions of the dead-stop end-point method and is a non-solvent for the pyridinium salts formed during the titration, it can be rendered sufficiently conducting and a solvent for the pyridinium salts by addition of about 25 per cent. of its volume of methyl alcohol; this condition is fulfilled during a titration by the addition of Fischer reagent (which contains methyl alcohol) provided that the volume added is sufficient. Pure dioxan or, where necessary, mixtures of dioxan with methyl alcohol were invariably used for the extraction of water from solids or the dissolution of solids; the proportion of dioxan in mixtures with methyl alcohol was always maintained as great as possible.

All solutions to be estimated were kept in stoppered measuring cylinders, reducing to a minimum the surface area of solution exposed to the atmosphere during withdrawal of an aliquot portion with a pipette. Using dioxan or mixtures of dioxan and methyl alcohol, it was not found necessary to provide for the exclusion of atmospheric moisture during the very short period of time required for the withdrawal. During the actual titration, however, such provision was essential and was achieved by passing a stream of dry nitrogen continuously into the titration vessel for the whole of the time the apparatus was in use; although the effect on the water content might have been negligible the stream of dry nitrogen was not allowed to bubble into the solution as this would have led to loss of iodine by vaporisation.

In order to increase the accuracy of the method for small quantities of water the use of a more dilute Fischer reagent was investigated and it was found that the reagent recommended by previous workers (including Smith, Bryant and Mitchell[4]) could be diluted without impairing the sensitivity of the method. The final solution adopted had a strength equivalent to about 1·5 mg. water per ml. The standard water solution for back-titration of the excess Fischer reagent was prepared from a 1 : 1 by volume mixture of methyl alcohol and dioxan and was approximately equivalent in strength to the Fischer reagent, *i.e.*, it contained about 1·5 mg. of water per ml.; standard water solutions prepared with a higher proportion of dioxan to methyl alcohol, including pure dioxan were found to be equally satisfactory. For the estimation of larger quantities of water, the stronger Fischer reagent can of course be employed and the water content of the stock water solution correspondingly increased. Finally, it was discovered that an e.m.f. of 200 mv. or even higher could be employed without any apparent decrease in sensitivity; to standardise procedure an e.m.f. of 80 mv. was used. In presence of some highly oxygenated substances the voltage must be kept very low, *e.g.*, not above 20 mv. for tetryl.

Method

Preparation of Reagents—

Pyridine is dried by allowing it to stand over anhydrous barium oxide for a few weeks, pouring off and distilling. Dioxan is dried by allowing it to stand over freshly heated calcium oxide for 3–4 days and filtering the supernatant dioxan through a sintered glass funnel with atmospheric moisture excluded. Methyl alcohol and iodine are used as AnalaR reagents.

The Fischer reagent is prepared by dissolving 84·7 g. of iodine in 667 ml. of methyl alcohol in a large round-bottomed flask, adding 269 ml. of pyridine and cooling in ice; 64 g. of liquid sulphur dioxide are weighed into a small beaker and carefully added to the iodine solution while shaking gently, the flask being closed after each addition with a bung carrying a calcium chloride tube. The solution is diluted with an equal volume of methyl alcohol and stored in a dark glass bottle.

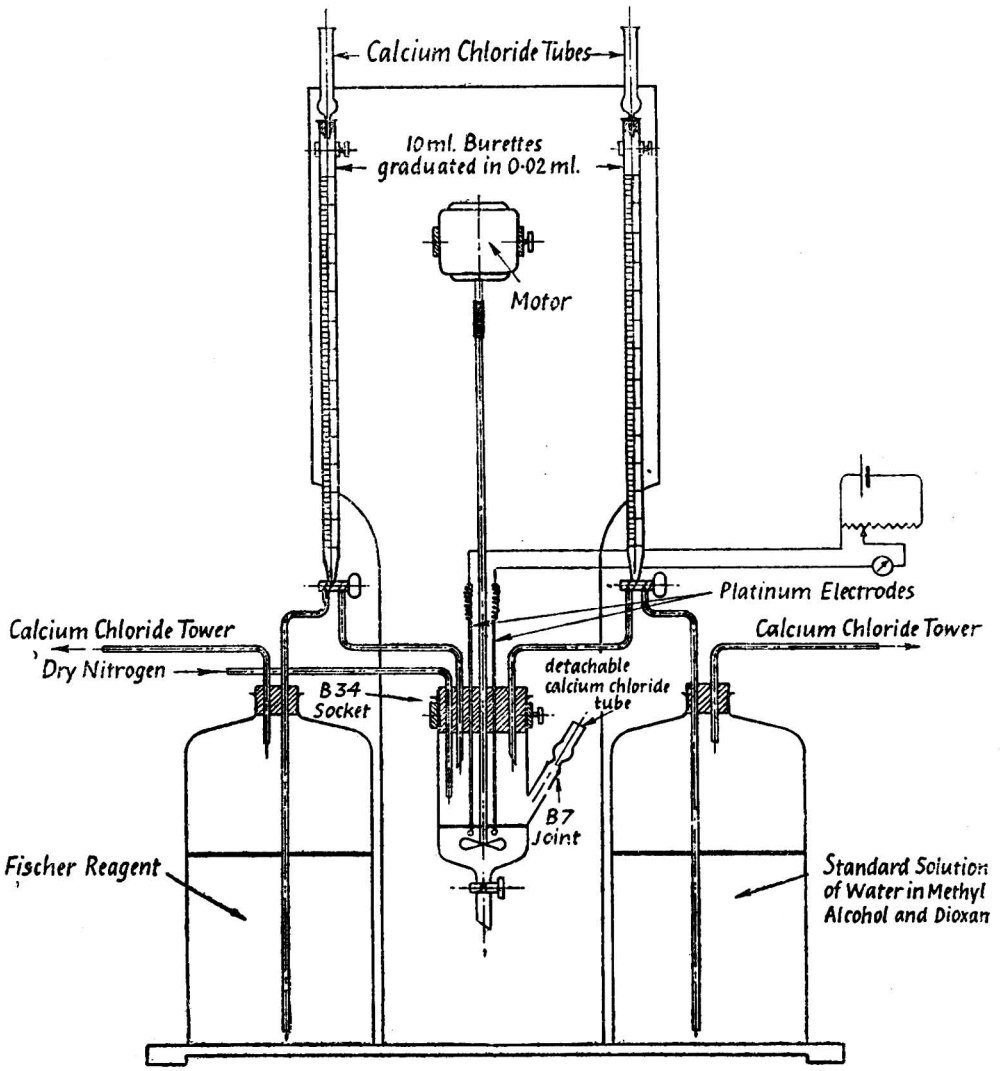
The standard solution of water is prepared by adding about 2·5 ml. of water to a mixture of 1 litre of methyl alcohol and 1 litre of dioxan (each of these solvents obtained as described above contain about 0·02–0·03 per cent. of water).

Apparatus—

The Fischer reagent and the standard water solution are separately contained in dark-coloured bottles forming part of the apparatus shown in the figure. Both solutions are pumped into the burettes by a hand bellows, the air passing into the bottles being dried by passage through a calcium chloride tower. The burettes are of 10 ml. capacity, graduated in 0·02 ml. and are closed by small calcium chloride tubes having a short length at the top of the tube filled with silica gel to prevent rapid "caking" of the calcium chloride; this involves no danger of loss of water from the standard water solution, which is very dilute. The titration vessel has a ground glass B.34 neck and a capacity of 60–70 ml. It carries a well-fitting bakelite stopper drilled with holes to take the two burettes, the two glass tubes with sealed-in platinum wires, the stirrer and an inlet tube attached to a drying train through which nitrogen from a cylinder of the compressed gas is passed continuously into the vessel; the drying train consists of a calcium chloride tower, two wash bottles containing concentrated sulphuric acid and a phosphorus pentoxide tube. All the tubes passing through the bakelite stopper are treated with sealing wax to give an air-tight seal and the stirrer and stopper are thickly coated with a suitable vaseline. The provision of a tap to allow titrated solutions to be run off and replaced by dry nitrogen avoids the necessity of removing the titration vessel after each titration and the exposure of the dry, hygroscopic solvent on the interior surface of the vessel to atmospheric moisture. The solutions to be estimated are introduced through the narrow side arm which at all other times is closed with a small calcium chloride tube, the end of which is ground to fit the B.7 ground glass neck of the side-arm. The bottles, the burettes, the electric motor for driving the stirrer and the titration vessel are mounted on a wooden stand and baseboard as shown. A self-contained portable potentiometer (Cambridge Instrument Co., No. L.25740) calibrated to 2 mv. was used to apply the e.m.f. of 80 mv. to the platinum electrodes, using a 1·5 v. dry battery as the source of supply. The connection between the platinum electrodes and the potentiometer is made in the usual way by filling the glass tubes with mercury. The pointer galvanometer of the unipivot type included in the output circuit has a sensitivity of 15 mv. per full scale deflection and was quite adequate for detecting the end-point of the titration.

STANDARDISATION OF THE STANDARD WATER SOLUTION—

After passing dry nitrogen into the titration vessel for 15 minutes, deliver 4 ml. of Fischer reagent into the vessel and apply an e.m.f. of 80 mv. to the platinum electrodes. With the galvanometer needle deflected off the scale, stir the solution and add the standard water solution until the colour approaches a yellowish brown. Then continue



the addition dropwise until the galvanometer needle "kicks"; stop the stirrer and the return of the needle to the zero point of the scale indicates the end-point of the titration. Run out the solution, deliver another 4 ml. of Fischer reagent into the vessel and titrate as before. Repeat until three successive titrations do not differ by more than 0·01 ml. During the titration the stirrer should not be allowed to rotate too rapidly, since its mechanical action is then liable to sweep away the hydrogen accumulating on the cathode at the end-point and so delay the movement of the galvanometer needle back to the zero of the scale.

Into each of two 50 ml. measuring cylinders provided with stoppers pipette 50 ml. of "dry" dioxan (*i.e.*, dioxan dried to a water content of 0·02–0·03 per cent. as described above) and stopper the flasks immediately. The dioxan should be drawn into the pipette by means of an air or water suction pump with a calcium chloride tower inserted between the pipette

and the source of suction. Into one of the measuring cylinders introduce a weighed quantity of water by means of a Lunge Rey pipette. Then titrate each of the two solutions in turn by withdrawing a 5 ml. portion in a pipette, introducing it into the titration vessel through the side arm, adding a measured excess of the Fischer reagent and titrating back the excess of Fischer reagent with the standard water solution as above. Repeat the titration until two successive values do not differ by more than 0·01 ml.

The amount of water in each of the two solutions is then expressible in ml. of the standard water solutions. The actual difference in water content of the two solutions is known since it is equal to the weight of water added to one, and this can be equated to the difference in ml. of standard water solution for the two solutions. The equivalence of the standard water solution to the weight of added water is thus established and its actual water content can be calculated. Usually another solution of a weighed amount of water in 50 ml. of "dry" dioxan was prepared and titrated to provide a check. It was found advisable on all occasions to add sufficient excess of Fischer reagent to give a back titration of at least 1 ml. of the standard water solution. An actual example is given to make this method of standardisation clear and to demonstrate the accuracy of the method.

(1) *Titration of Fischer reagent* (*F.R.*) *against standard water solution* (*S.W.S.*):
1 ml. of F.R. ≡ 1·33 ml. of S.W.S. .. .. (i)

(2) *Titration of* 5 *ml. of "dry" dioxan*:
F.R. added, 3 ml.; S.W.S. required for back titration, 2·90 ml.

From (i), 3 ml. of F.R. ≡ 3 × 1·33	=	3·99 ml. of S.W.S.
Back titration	=	2·90 ml. ,, ,,
∴ Water in 5 ml. of "dry" dioxan	≡	1·09 ml. ,, ,, ... (ii)

(3*a*) *Titration of* 5 *ml. of dioxan containing* 0·01396 *g. of added water*:
F.R. added, 8·50 ml.; S.W.S. required for back titration, 1·12 ml.

From (i), 8·50 ml. of F.R. ≡ 8·50 × 1·33	=	11·30 ml. of S.W.S.
Back titration	=	1·12 ml. ,, ,,
∴ Total water in the dioxan solution	≡	10·18 ml. ,, ,,
From (ii), water originally in the dioxan	≡	1·09 ml. ,, ,,
∴ The added water, 0·01396 g.,	≡	9·09 ml. ,, ,,

Hence **1 ml. of S.W.S. ≡ 0·01396/9·09 ≡ 0·00154 g. of water.**

(3*b*) A similar titration to (3*a*) but with 0·0151 g. of added water, gave
1 ml. of S.W.S. ≡ 0·00155 g. of water

If at any stage during the standardisation it is found necessary to detach the Fischer titration vessel, *e.g.*, through blockage of a burette, it is essential on replacing the vessel to titrate again 4 ml. portions of the Fischer reagent with the standard water solution as described in the first part of the determination; this titration is repeated until the original relationship between the two solutions is established. Only when this is achieved can the standardisation be resumed at the point where the vessel was detached.

Since the Fischer reagent gradually decreases in strength, it is essential to standardise it by titration against the standard water solution daily, and the latter should be standardised by the procedure described above at least once per week.

Results of estimations of dioxan solutions of known water content prepared by adding weighed quantities of water to "dry" dioxan are given in Table I. The results indicate an accuracy of 2–3 per cent. over the range 3–15 mg. of water.

Effect of Atmospheric Moisture—

The effect of atmospheric moisture in the Fischer method was investigated by (1) standardising the standard water solution as above at two different relative humidities and (2) repeating the standardisation at the same two relative humidities but without passing dry nitrogen into the titration vessel. The two relative humidities were 47 per cent. and 89 per cent. The results are shown in Table II. In the column headed "Factor" is given the volume in ml. of standard water solution equivalent to 4 ml. of Fischer reagent, while the last column, headed "Strength of S.W.S.," is the amount of water per ml. of the standard

water solution as found by standardisation. It is clear that with a relative humidity of 47 per cent. no interference from atmospheric moisture occurs when "dry" nitrogen is not passed into the titration vessel. With the relative humidity at 89 per cent., however, the effect of atmospheric moisture, in the absence of the dry nitrogen, is to reduce the effective strength of the Fischer reagent relative to the standard water solution by about 5 per cent. and to result in an error in the estimation of the strength of the standard water solution. Since the apparatus is designed to reduce exposure to atmospheric moisture to a minimum (quite apart from the employment of dry nitrogen) it is evident that any method involving detachment of the titration vessel during a series of estimations is liable to an even greater error, varying with the prevailing humidity.

TABLE I

WEIGHED AMOUNTS OF WATER IN DIOXAN SOLUTION

Weight of water added to 5 ml. of dioxan g.	Weight of water found g.	Error %
0·0155	0·0158	+1·8
0·0153	0·0154	+0·7
0·0128	0·0126	−1·8
0·0103	0·0102	−1·0
0·0101	0·0102	+1·0
0·0095	0·00935	−1·6
0·0052	0·00534	+2·8
0·00364	0·00360	−1·7
0·00314	0·00304	−3·3
0·00294	0·00286	−2·8

TABLE II

EFFECT OF ATMOSPHERIC MOISTURE

	Relative humidity	Factor	Strength of S.W.S.
Passing dry nitrogen ..	47	2·00	0·00266
	89	1·98	0·00264
Not passing dry nitrogen	47	1·99	0·00265
	89	1·89	0·00273

ANALYSIS OF THE WATER CONTENT OF PROPELLANTS

The high viscosity of solutions of nitrocellulose, which is the principal constituent of propellants, precludes the use of nitrocellulose solvents for the dissolution of the water in propellant samples. To overcome this difficulty, attempts were made to free the water by heating under reflux and distilling the sample with dioxan in an all-glass apparatus. The end of the condenser was connected to a 50 ml. measuring cylinder by means of a suitable adapter, to which was attached a calcium chloride tube to exclude atmospheric moisture. 2–3 g. of the propellant sample, prepared by breaking or cutting into small pieces, was added to 50 ml. of dioxan in a 150 ml. conical flask, and refluxed gently in the apparatus for about 20 minutes; the major portion (about 35 ml.) of the dioxan was then allowed to distil over slowly into the measuring cylinder. The procedure was repeated with 50 ml. of dioxan without the sample, and the water content of each of the solutions determined. The method was found to be satisfactory except that occasionally the propellant decomposed with liberation of water. During the distillation it was observed that the propellant grains became slightly swollen in appearance and further investigation revealed that if the sample was allowed to stand in contact with dioxan overnight, the dioxan penetrated into the propellant grains and completely extracted the water without causing dissolution of the propellant (which would have resulted in the formation of a viscous solution). The method finally adopted therefore was to add 25 ml. of "dry" dioxan to a 2–3 g. sample of propellant in a 25 ml. measuring cylinder, which was stoppered and allowed to stand overnight. The water content of the supernatant dioxan was then determined on 5 ml. aliquots. The water content of the "dry" dioxan was also determined and the percentage of water in the sample calculated. The results of determinations on several different types of propellants are given in Table III and are compared with the water content as determined on 25 g. quantities of the samples by an adaptation of the entrainment method of Dean and Stark[11] (*i.e.*, removal of the water

by distillation from a solution of the sample in acetophenone with benzene and direct measurement of the volume of water collected). Excellent agreement is evident. The propellants investigated variously contained nitrocellulose, nitroglycerine, diethyldiphenylurea, nitroguanidine, dinitrotoluene, dibutyl phthalate and mineral jelly.

TABLE III

WATER IN PROPELLANTS

Sample 2 g./20 ml. of dioxan	Wt. of water in 5 ml. aliquot of dioxan g.	Water found %	Water found by Dean and Stark method %
NH powder, web size 050	(I) 0·00520 (II) 0·00518 (III) 0·00504	(I) 1·04 (II) 1·04 (III) 1·01	1·05
NH powder, web size 033	(I) 0·0046 (II) 0·00465	(I) 0·92 (II) 0·93	0·95
Cordite WM 130	(I) 0·0020 (II) 0·0020	(I) 0·40 (II) 0·40	0·40
Cordite containing nitroguanidine ..	(I) 0·0012 (II) 0·0011	(I) 0·24 (II) 0·22	0·25
Solventless cordite	(I) 0·00285 (II) 0·0028	(I) 0·57 (II) 0·56	0·55

Other solid substances that are not as heat-sensitive as propellants can be successfully treated by the method of distilling with dioxan, and substances which dissolve completely in dioxan or methyl alcohol - dioxan mixtures can be titrated directly after dissolution. Direct titration of insoluble substances by introducing a weighed amount of the solid through the side arm of the Fischer titration vessel gave erratic results in the few cases investigated, *e.g.*, starch, but this method may be successful for some substances and should always be investigated. To the group of substances which interfere in the Fischer reaction should be added boric acid, which has been found to esterify the methyl alcohol present with liberation of a nearly quantitative yield of water.

SUMMARY

An improved method and apparatus is described for employing the Fischer reagent for the estimation of quantities of water of the order of a few milligrams. Atmospheric moisture is excluded by passing a stream of dry nitrogen gas into the vessel used for titration, and the value of this innovation is demonstrated by ascertaining the effect of different relative humidities on titrations with and without the employment of dry nitrogen gas. The method has been successfully used for the estimation of water in propellants and other explosives.

In conclusion I should like to thank Mr. G. L. Hutchison, of the Armament Research Department, for his valuable advice on the problem of estimating the water content of propellants and the Chief Scientific Officer, Ministry of Supply, for permission to publish this material.

Acknowledgment is made to the Chemical Inspection Department, Ministry of Supply, whose staff independently suggested the use of the side tube in the reaction vessel as an alternative to a tube through the stopper.

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ARMAMENTS RESEARCH DEPARTMENT
MINISTRY OF SUPPLY
WALTHAM ABBEY, ESSEX

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Discussion

Mr. N. Strafford enquired how the standard water solution was prepared and standardised and whether its water content altered on storage. He also confirmed the experience of American workers (*cf.* G. C. Warren, *Canad. Chem. Process Inds.*, 1945, **29**, 370; *Chem. Abstr.*, 1945, **39**, 3221), who had recommended the use of hydrated sodium acetate ($3H_2O$) as a convenient substance for the standardisation of the Fischer reagent.

Dr. H. E. Cox enquired whether the author had found the method suitable for determining water in fatty oils and whether polyhydroxyl compounds, such as glycols or glycerol or even higher alcohols such as propanol, interfered.

Mr. J. H. High asked if there was any objection to the use of nitrogen to stir the mixture during titration.

Mr. A. H. Holloway mentioned that the end-point might be approached by titrating the water with the Fischer reagent, in which case a fading end-point was observed, or by adding an excess of reagent and titrating back with standard water in methanol, in which case a definite end-point, the "dead-stop," was obtained. In the estimation of small quantities of water these end-points in many cases did not agree with one another or with the visual end-point. Had the author any observations on this point, and did he think that the dead-stop end-point was well defined, because it was, in fact, overshot?

Mr. J. Haslam asked if the author had any experience of the Carter and Williamson method (Analyst, 1945, **70**, 369) in which a direct titration of the water was carried out.

Mr. R. C. Chirnside asked the author if he thought the method would be applicable to two of the commoner refrigerants, liquid sulphur dioxide and methyl chloride. The first of these was of course one of the constituents of the Fischer reagent. The quantities of water involved were of the order of 50 parts per million.

In a written communication, Mr. N. L. Allport, who was unable to attend the meeting, said he had been privileged some time ago to visit the author's laboratory and see the procedure for determining moisture actually being carried out. He had been much impressed by the manner in which the defects associated with the Fischer method had been eliminated. Since then his colleagues at the B.D.H. Laboratories had set up the equipment described in this paper and had found the method quite satisfactory. He considered that the modifications proposed effected most significant improvements in the Fischer method and he felt that analysts were indebted to the author for a most useful advance.

Mr. T. G. Bonner, in reply to Mr. Stafford's question, stated that full experimental details of the preparation and standardisation of the standard water solution were given in the paper; solutions of known weights of water in dioxan were employed in place of hydrated salts. In reply to Dr. Cox, he said that the Fischer reagent had been used for pine oil and no difficulties should arise in the case of fatty oils; neither polyhydroxyl compounds nor higher alcohols interfered and he had used the method with diethylene glycol and glycerol in the normal way. Replying to Mr. High, he stated that the only objection to passing the nitrogen directly into the mixture for the purpose of stirring was that the methyl alcohol readily vaporised, leaving a deposit of pyridinium salts on the walls of the titration vessel. Replying to Mr. Holloway and Mr. Haslam, he referred to the fact that many workers had reported the fading end-point when the Fischer reagent was directly titrated against water and in view of this phenomenon it was unwise to expect agreement with the described method of adding excess of Fischer reagent and titrating back the excess with a standard solution of water; in explanation of the fading end-point he suggested that the sensitivity of the Fischer reagent to atmospheric moisture and the general failure of workers to prevent interference were partly responsible, since the gradual take-up of atmospheric by the very slight excess of Fischer reagent present at the end-point of the direct titration would tend to cause fading of the end-point. In the method now described the dead-stop end-point is most well defined and sensitive to 0·01 ml. of the standard solution containing 1·5 mg. of water per ml. In reply to Mr. Chirnside, the author stated that the method had been originally developed by Fischer for the estimation of water in liquid sulphur dioxide and it was doubtless equally applicable to methyl chloride; in 1945, a method had been reported in *Ind. Eng. Chem., Anal. Ed.*, for the estimation of 0–60 parts per million of water in petroleum fractions, in which 150 ml. samples were used.

Notes

THE DETERMINATION OF IRON IN CEREALS

A recent paper gives figures for the iron content of flours of different extraction milled from the same grist of wheat or rye.[1] Wheats vary in their iron content, and during milling the products may pick up traces of iron from the plant.[2] For both reasons, therefore, the iron contents of samples of flour of given extraction are not constant.

Iron is an important nutrient in cereal grains, and work is in progress in these laboratories on its distribution in wheat, oats and other cereals. Meanwhile the analytical method we are at present employing may be of interest.

Reagent—Of the many reagents that have been used for the estimation of small quantities of iron in biological material those containing the cyclic N–C–C–N grouping which form co-ordination complexes with ferrous iron are preferable because of their specificity, the wide *p*H range over which they can be used and their sensitivity. With the introduction of 2:2′-dipyridyl by Hill,[3] 2:2′:2″-tripyridyl by Cooper,[4] 1:10-phenanthroline by Saywell and Cunningham[5] and five new derivatives of 1:10-phenanthroline by Moss, Mellon and Smith,[6] a wide choice has become available. The absorption spectra of the ferrous complexes of these

reagents and the effect on them of many diverse ions have been studied, the data given in the table below have been abstracted from these papers.[6, 7, 8]

Reagent	Applicable *p*H range	Wave length of max. absorption mμ	Molecular extinction coefficient
2:2′-Dipyridyl	3–9	522	8,650
2:2′:2″-Tripyridyl	3–10	552	11,500
1:10-Phenanthroline	3–9	510	11,100
$5NO_2$-6-Me-1:10-Phenanthroline ..	3–8	512	12,400

Only dipyridyl and *o*-phenanthroline are at present available commercially, and the latter reagent was selected for use in these laboratories because it is about 28 per cent. more sensitive than the former. This reagent is also used by the A.O.A.C. for the determination of iron in plant ashes and cereal foods.[14] When in solution it should be stored in the dark.

Ashing—Howe[9] and Andrews and Felt[10] have shown that, compared with wet ashing, dry ashing of the sample does not cause any apparent loss of iron. The dry ashing procedure was therefore adopted and the extraction of the ash carried out by a method based on that of Cowling and Benne.[11] The hydrofluoric acid treatment of the ash advocated by these authors is not necessary for wheat and rye and their products, but should be carried out for any barley and oat product containing an appreciable amount of husk because of its high silica content.

Reducing Agent—Many substances have been proposed for reducing the ferric iron to the ferrous state. It has been stated[7] that a 10 per cent. solution of hydroxylamine hydrochloride is the most satisfactory, but we have found that this chemical is often contaminated with iron and gives rise to a high blank value. A 2 per cent. solution of sulphur dioxide in water is satisfactory, being comparatively stable and practically free from iron. Its strength may be checked periodically as suggested by Koenig and Johnson.[12]

Adjustment of p*H*—Accurate adjustment of the *p*H as in the method of Cowling and Benne[11] is not necessary in view of the wide *p*H range of the phenanthroline reagent. A considerable saving in time may be achieved by titrating the test aliquot itself with the sodium acetate solution, using a small square of Congo Red Paper for an indicator as in the original method.[5]

Procedure—The weighed sample (containing between 0·05 and 0·4 mg. Fe) is placed in a silica basin, 10 ml. of a 1:1 mixture of glycerine and alcohol are added and, after a preliminary burning-off at the entrance to the muffle furnace, it is ashed overnight at 600° C. After cooling, a measured quantity (0·5 to 1·0 ml.) of concentrated nitric acid is added to the ash, and evaporated off at the muffle entrance and the basin is replaced in the furnace for an hour. This removes the last traces of carbon. The cool ash is taken up in 5 ml. of a diluted hydrochloric acid (1+1), heated on a steam bath for 15 minutes to hydrolyse pyrophosphate, and filtered through an acid-washed hardened paper into a 100-ml. graduated flask. Three ml. of diluted hydrochloric acid (1 in 100) are put into the basin, brought to the boil on a hot plate and passed through the filter. This is repeated four times more and then the basin and filter are washed with hot water.

After making to volume and mixing, a 10-ml. aliquot of the ash solution is pipetted into a 25-ml. flask. One ml. of a 2 per cent. solution of sulphur dioxide is added and then a small square of Congo Red paper and the mixture is titrated with 2 *M* sodium acetate solution, which is added drop by drop from a burette until the change of colour (blue to pink). Two ml. of a 0·25 per cent. solution of *o*-phenanthroline in water (the hydrochloride is readily soluble but the monohydrate may require warming to effect solution) are then added and, after mixing and making to volume, the solution is left overnight to ensure full development of the colour. This is necessary because orthophosphate exerts a delaying action on the colour formation. The order of addition of the reagents is not critical when this procedure is adopted (see Bandemer and Schaible[13]).

The coloured solutions are read against a blank solution prepared in exactly the same manner as the test solutions, fresh blank solutions being prepared whenever fresh reagents are made up. Cells of 4 cm. depth are used in the Hilger Absorptiometer and Ilford No. 604 Spectrum Green filters with a maximum transmission at 520 mμ are used together with Hilger H 503 heat absorbing glass filters. The concentration of iron in the test solution is obtained by reference to a graph constructed from data obtained by the use of a standard iron solution containing 5 μg. of iron per ml.

To ensure freedom from contamination with iron the following precautions are necessary. The water used throughout should be redistilled from glass. All glass apparatus should first be soaked in chromic acid, then rinsed with dilute hydrochloric acid and finally rinsed with redistilled water. All reagents should be of AnalaR grade. No instruments made of iron or steel should be used either for weighing or handling the ash basins. To avoid grinding grain samples these are ashed whole, a preliminary drying in an electric oven at 100 to 120° C. overnight being necessary to prevent loss by explosion of the grains when the sample is placed in the furnace. Finally all containers, etc., should be covered to prevent as far as possible the entry of dust.

Accuracy—In a series of ninety samples of commercially-milled flour, the duplicate figures differed by more than 5 per cent. in only ten instances. Repeat determinations were carried out on these samples and in all except two the new figure was within 3 per cent. of the lower figure obtained in the original determination. It is probable, therefore, that in eight out of ten instances erratic results were due to the sample being contaminated with iron.

Of the eighty samples that were not repeated (*i.e.*, gave duplicate figures within 5 per cent. of each other) the duplicate figures for 86 per cent. differed by 3 per cent. or less and those for 72·5 per cent. differed by 2 per cent. or less.

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RESEARCH ASSOCIATION OF BRITISH FLOUR MILLERS,
CEREALS RESEARCH STATION, ST. ALBANS

W. J. S. PRINGLE
16th July, 1946

Official Appointments

Dr. J. R. NICHOLLS, F.R.I.C., has been appointed Deputy Government Chemist.

Dr. D. C. GARRATT, B.Sc., F.R.I.C., has been appointed Analyst to the Port of London Authority.

Mr. A. SCIVER, B.Sc., F.R.I.C., has been appointed Analyst to the Thames Conservancy.

PUBLIC ANALYST APPOINTMENTS

The following appointments of Public Analysts have been made since the last notification in THE ANALYST (1944, **69**, 16).

Public Analysts	*Appointments*
BRANSON, Victor Cecil (Deputy)	Western Division of Sussex County.
BUTTON, Donald Frank Harrington ..	Metropolitan Borough of Southwark.
CAVELL, Alan James (Deputy)	County Borough of Southampton.
CHILDS, Hugh	Cities of Lincoln, Sheffield and York, County Boroughs of Barnsley, Doncaster, Grimsby and Rotherham, and Boroughs of Chesterfield and Scunthorpe.
CLARK, James Frederick	City of Liverpool, County Boroughs of Barrow-in-Furness, Birkenhead, Blackburn, Bootle and Southport and Boroughs of Crosby and Widnes.
EVANS, Herbert John	County of Cardigan.
HERD, Magnus (Additional)	City of Glasgow.
HERON, Neil (Deputy)	City of Portsmouth.
HOULBROOKE, Albert	County of Stafford, City of Stoke-on-Trent, Boroughs of Newcastle-under-Lyme and Rowley Regis and Urban District of Brierley Hill.
JAMIESON, Archibald Robert	City of Glasgow.
JENKINS, Daniel Ceiriog	County Borough of Burnley.

JONES, Archibald Orton (Deputy)	City of Sheffield and County Boroughs of Rotherham and Grimsby.
JONES, Daniel Evans	County of Glamorgan, Borough of Port Talbot and Urban Districts of Aberdare, Pontypridd and Rhondda.
LEATHER, Alfred Norman	City of Salford and Boroughs of Eccles and Stretford.
LEES, Arnold (Deputy)	County Borough of Preston, Boroughs of Leigh (Lancs.) and Morecambe & Heysham and Urban District of Newton-le-Willows.
LOVE, Malcolm McFarlane	County and City of Worcester and Boroughs of Kidderminster and Oldbury.
LYNE, Francis Arthur (Deputy)	County of Berkshire and County Borough of Reading.
McHUGO, Christopher William (Deputy) ..	County of Middlesex.
McKEAN, John Brown	County of Lanark and Burghs of Dumbarton and Paisley
MINOR, Roland Gordon (Deputy)	Metropolitan Borough of Southwark.
MOIR, Daniel Donald	County of Surrey, County Borough of Croydon, Boroughs of Barnes, Esher, Guildford, Kingston-upon-Thames, Malden & Coombe, Mitcham, Reigate, Sutton & Cheam, and Wimbledon, and Urban Districts of Carshalton and Merton & Morden.
MONK, Harold Edward	County of Kent, Boroughs of Beckenham, Bexley, Bromley, Chatham, Dartford, Erith and Gillingham and Urban Districts of Chislehurst & Sidcup and Orpington.
MUNDY, Lilian Marjorie	Counties of Ayr and Renfrew and Burghs of Ayr and Kilmarnock.
RITCHIE, John Edwin ROBB, Marshall Jeffreys } (Joint) ..	Counties of Aberdeen, Banff, Caithness, Kincardine, Ross & Cromarty and (interim) Inverness and Sutherland.
ROBERTS, Muriel (Deputy)	Borough of Widnes.
TAYLOR, William Wilders	County of Nottingham.
,, ,, ,, (Additional) ..	Lindsey Division of Lincolnshire.
VOELCKER, Eric	County of Middlesex and Borough of Slough.
WALKER, George Hugh	County of Lancashire, County Borough of Preston, Boroughs of Chorley, Darwen, Leigh (Lancs.) and Morecambe & Heysham and Urban District of Newton-le-Willows.
WATRIDGE, Roy Warren	Southampton and the Isle of Wight and the City of Winchester.
WHITTLE, Ernest George (Deputy)	City of Bristol.
WILLIAMS, Albert Lester	City of Portsmouth.
WORDSWORTH, Charles Harcourt	Borough of Bedford and Metropolitan Boroughs of Finsbury, Holborn and St. Pancras.
WRIGHT, Reginald Frank	County Borough of Hastings.

OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

The following appointments of Official Agricultural Analysts have been made since the last notification in THE ANALYST (1945, **70**, 51).

Official Agricultural Analysts	*Appointments*
CHILDS, Hugh	County Boroughs of Barnsley, Doncaster, Grimsby, Lincoln, Rotherham, Sheffield and York.
CLARK, James Frederick	County Boroughs of Birkenhead, Blackburn, Bootle, Liverpool and Southport.
EVANS, Herbert John	County of Cardigan.
HOULBROOKE, Albert	County of Stafford and County Borough of Stoke-on-Trent.
JAMIESON, Archibald Robert	County Burgh of Glasgow.
JENKINS, Daniel Ceiriog	County Borough of Burnley.
JONES, Archibald Orton (Deputy)	County Boroughs of Grimsby, Rotherham and Sheffield.
JONES, Daniel Evans	County of Glamorgan.
LEATHER, Alfred Norman	County Borough of Salford.
LEES, Arnold (Deputy)	County of Lancashire and County Borough of Preston.
LOVE, Malcolm McFarlane	County and County Borough of Worcester.
LYNE Francis Arthur (Deputy)	County of Berkshire and County Borough of Reading.
MOIR, Daniel Donald	County of Surrey and County Borough of Croydon.
MONK, Harold Edward	County of Kent.
MUNDY, Lilian Marjorie	Counties of Ayr and Renfrew and Burghs of Ayr and Kilmarnock.
RITCHIE, John Edwin ROBB, Marshall Jeffreys } (Joint) ..	Counties of Aberdeen, Banff, Caithness, Kincardine, Ross & Cromarty and (interim) Inverness and Sutherland.
TAYLOR, William Wilders	County of Nottingham.
WALKER, George Hugh	County of Lancashire and County Borough of Preston.
WATRIDGE, Roy Warren	County Borough of Southampton and Isle of Wight.
WHITTLE, Ernest George (Deputy)	County Borough of Bristol.

Ministry of Food

STATUTORY RULES AND ORDERS

1946 No. 1261. The Feeding Stuffs (Maximum Prices) Order, 1946. Dated July 25, 1946. Price 10d.

This 40-page consolidating Order revokes and substantially re-enacts the Feeding Stuffs (Maximum Prices) Order, 1943 (S.R. & O., 1943, No. 1497), as amended by subsequent Orders (1944, Nos. 313, 797 and 1349; 1945, Nos. 878 and 1472; 1946, No. 661).

— **No. 1416. Order, dated August 21, 1946, amending the Feeding Stuffs (Regulation of Manufacture) Order, 1944.** Price 2d.

This Order, which came into force on August 26, 1946, makes provision for the use of cod liver oil of a high vitamin A potency in National Poultry Foods Nos. 1A and 2A and in National Baby Chick Food. It prohibits the use of cod-liver oil in all other compounds, concentrates and mixtures. It also amends the oil and albuminoid contents of National Cattle Foods Nos. 1 and 3.

The Unification of Pharmacopoeias

INTERIM REPORT OF THE TECHNICAL COMMISSION OF PHARMACOPOEIAL EXPERTS*

APPOINTED IN 1937 BY THE HEALTH ORGANISATION OF THE LEAGUE OF NATIONS

THE following is an abridged account of the Report, to which we have been asked to draw attention.

The value of uniformity in the various National Pharmacopoeias has long been recognised and the necessity for unification of the standards for drugs and of the strengths and formulae of preparations, through the medium of an International Pharmacopoeia, has been stressed by many workers in this field. There is a desire for a uniform system of nomenclature, and it is specially urged that the same name should, in all countries, designate a drug of the same strength and composition. Differences in national standards for widely used materials constitute a source of danger to travellers who may need to have the same prescription dispensed in different countries, not only because of the possible supply of a drug differing in strength from that to which the patient is accustomed, but also because of delays in receiving medicines that may have to be specially made or procured. Such differences, by causing confusion and misunderstanding, are also a hindrance to the spread of medical and pharmaceutical knowledge. A state of affairs under which the same supply of a drug or chemical may be accepted in one country and rejected in another may lead to the retention of lower standards in manufacture, whilst the maintenance of a common high standard would tend to economy of production and would facilitate commerce between the nations. The desire for the unification of terminology and of the strengths and composition of medicines led, in the years between 1874 and 1902, to attempts to produce an International Pharmacopoeia. In 1902, a Conference called by the various Governments was held and the First International Agreement for the Unification of the Formulae of Potent Drugs was drawn up. This Agreement was ratified in 1906, and considerably influenced the national Pharmacopoeias subsequently published.

A Second International Agreement was produced at a Conference held at Brussels in 1925, and was completed in 1929. This Agreement consists of forty-one articles, and deals with such subjects as the general principles for the preparation of galenicals, a definition of a standard "dropper," biological testing of the arsenobenzenes, nomenclature and maximal doses. The main practical interest centres in Article 8, which contains a table of the strengths and descriptions of 77 potent drugs and preparations. Other articles are designed to provide for an international organisation for the unification of Pharmacopoeias, with a permanent secretariat which would have the duty of co-ordinating the work of the national Pharmacopoeia Commissions. It was the intention, expressed in Article 35, that the League of Nations should take up the administration of this work, the Belgian Pharmacopoeia Commission acting meanwhile as the central secretariat. Other articles provide for the formation of two special Commissions, one for the international study of the unification of methods for the chemical and physico-chemical assay of potent remedies, and the other for the unification of the methods of preparing potent galenicals.

In response to the frequently expressed desire of pharmacopoeial workers in various countries to the effect that this Agreement should be revised and extended to cover a limited International Pharmacopoeia, the Health Organisation of the League of Nations set up, in 1937, a Technical Commission of Pharmacopoeial Experts. This Commission, which was formed after negotiation with the Belgian Government and in liaison with the International Pharmaceutical Federation, was constituted as follows: Dr. C. H. Hampshire, Secretary, British Pharmacopoeia Commission (*Chairman*); Professor H. Baggesgaard-Rasmussen, of the Pharmazeutiske Laereanstalt, Copenhagen; Dr. E. Fullerton Cook, Chairman of the Committee of Revision of the Pharmacopoeia of the United States of America, Philadelphia; Professor R. Eder, Director of the Pharmaceutical Institute of the Polytechnicum, Zurich; Professor M. Tiffeneau, Dean, Faculty of Medicine, Paris; Professor L. Van Itallie, Director of the Institute of Pharmacy, Leyden; and Professor Edgar Zunz, Laboratory of Pharmacodynamics and Therapeutics, University of Brussels.

This Commission was charged with the duty of preparing a draft of a new International Agreement to be submitted to the various Governments through the Belgian Government.

The first meeting was held at Geneva in May, 1938, when the existing Agreement was reviewed and the scope and general plan of the work to be done were agreed upon and a committee of Galenical Pharmacy formed. The members agreed that the best method of achieving the objects desired would be to prepare a draft Agreement including: (*a*) General Rules relating to Nomenclature, Strengths of Galenicals and other

* Bulletin of the Health Organisation of the League of Nations, Vol. XII, Extract No. 4, 1945–46.

medical and pharmaceutical matters, (*b*) a table of Usual and Maximal Doses, (*c*) monographs on important drugs which are common to a number of the national Pharmacopoeias.

The second meeting took place in Geneva in May, 1939, when draft monographs and reports on 73 drugs were submitted by members for discussion. The draft monographs accepted are printed in Section 4 of this report. The Commission gave considerable attention to the form of the monographs and decided to adopt the following general principles: every part of each monograph to have an official character unless otherwise stated; the description of each test to be preceded by a sub-heading indicating the nature or purpose of the test; graphic formulae of organic compounds to be included in all suitable cases, as providing the most precise definition; sections to be added, as required, on Storage, Sterilisation and Doses.

A draft list of Usual and Maximal Doses was discussed and adopted. This is printed in Section 3 of the present Report. A further programme of work was arranged, including the drafting of additional monographs, and the laboratory investigations necessary in order to resolve difficulties encountered in the revision of the monographs considered at the meeting.

A third meeting projected for September, 1940, was abandoned in consequence of the European War. Many draft monographs and reports must await another meeting of the Commission, but it is advisable, in the present circumstances, to place on record, in the form of an Interim Report, some account of the results already accomplished. This Report presents certain suggested general rules, a list of doses, a sufficient selection of completed monographs to indicate the proposed style and contents, and a list of the other drugs under study, thereby outlining the scope of a limited International Pharmacopoeia as envisaged by the Commission at its first meeting. In making its first selection of drugs for description, the Commission realised that some machinery would be necessary to enable new drugs to be added, from time to time, to the list, and it is obvious that numerous drugs, such as the sulphonamides, penicillin and the synthetic antimalarials, which have proved their value during the war, should be considered at a future meeting of the Commission. The task of the Commission is thus seen to be as yet far from completed.

The Commission has lost by death three valued members: Professor E. Eder, Professor E. Zunz and Professor M. Tiffeneau. The present Interim Report is presented with the agreement of the surviving members, as an account of the work that has been accomplished and an indication of the lines on which future work should proceed.

It contains five sections, *viz.*,

Section 1, pp. 3–7—Historical and General.

Section 2, pp. 8–9—General Rules, relating to Nomenclature and Galenicals and Specification of a Standard Dropper to deliver drops of distilled water weighing 0·50 ± 0·01 g. at 15°.

Section 3, pp. 10–13—A Table of Usual and Maximal Doses of 104 drugs, giving in separate columns name of drug, mode of administration, usual dose and single and daily maximal doses.

Section 4, pp. 14–67—Monographs on 47 drugs.

Section 5, pp. 68–70—Additional List of 160 Drugs under study for inclusion in an International Pharmacopoeia.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Biochemical

Cerimetric Determination of Glucuronic Acid, using the Conway Burette. G. A. Levvy (*Biochem. J.*, 1946, **40**, 396–400)—To 0·8 ml. of a solution containing not more than 300 μg. of glucuronic acid in a 10 ml. centrifuge tube, add 0·6 ml. of a 2·5% solution of $CuSO_4.5H_2O$ and, after mixing, 0·6 ml. of a 2·5% solution of $Na_2WO_4.2H_2O$ in 0·5% sodium carbonate solution. Shake vigorously, add about 10 mg. of powdered barium carbonate, leave for 10 min., again shake and then centrifuge. Transfer 1 ml. of the supernatant solution to another 10 ml. centrifuge tube, add 0·25 ml. of a freshly prepared mixture (1 : 10) of 5% potassium ferricyanide solution and 11% sodium carbonate solution and, after closing the mouth of the tube with a glass bulb, immerse in a boiling water-bath for 15 min. Cool, add 0·2–0·25 ml. of 11 *N* sulphuric acid and 1 or 2 drops of 0·03% Setopaline C indicator and immediately titrate with 0·012 *N* ceric sulphate solution (10 ml. of the 0·3 *N* solution diluted to 250 ml. after addition of 23 ml. of 11 *N* sulphuric acid) from a Conway burette with air stirring by means of a capillary tube attached to the burette jet. The colour change is from yellow or greenish yellow to red-brown and the end-point should be stable for at least 30 sec. A blank estimation is carried out on the reagents and the result is subtracted from the titre obtained with the test solution. The ceric sulphate solution is standardised against ferrous ammonium sulphate solution. Since the reaction between glucuronic acid and potassium ferricyanide does not follow a linear relationship the glucuronic acid equivalent of the ceric sulphate solution has to be determined for the conditions employed. By carrying through the above procedure with known amounts of *d*-glucurone, it was found experimentally that 1 μg. of glucuronic acid is equivalent to 0·002 ml. of 0·0124 *N* ceric sulphate solution. In a series of 28 determinations in which 99·5 μg. of glucuronic acid were added to an enzyme preparation, the mean recovery was 95·0 μg. and the standard deviation of a single observation from the mean was 2·4 μg. F. A. R.

Cerimetric Determination of Blood Glucose. R. H. Nimmo-Smith (*Biochem. J.*, 1946, **40**, 414)—Put 0·1 ml. of blood into a clean 10 ml. centrifuge tube containing 0·9 ml. of water and, after laking is complete, add 0·5 ml. of each of the protein precipitants recommended by Levvy (see preceding abstract) followed by solid barium carbonate. If larger quantities of blood are available, add 0·5 ml. to 2 ml. of water and add 2 ml. quantities of the protein precipitants. After adding the barium carbonate, leave for 10 min., dilute to 10 ml. and then centrifuge for 5 min. at 3,800 r.p.m. Use 1 ml. of the supernatant liquid for the estimation of glucuronic acid as described by Levvy (see preceding abstract). If Setopaline C is not available use *o*-phenanthroline ferrous complex or, better, a 0·05% solution of Lissamine green (BDH) which gives a similar colour change. One μg. of glucose was found to be equivalent to 0·002 ml. of 0·0140 *N* ceric sulphate, so that

glucose has a slightly greater reducing power than glucuronic acid. With a sample of blood giving 27·0 μg. per ml. in the supernatant liquid, the standard deviation was ± 0·76 μg., and with blood giving 100 μg. per ml. it was ± 0·79 μg. The recoveries of glucose, added to blood in amounts of 25·2 and 100·8 mg. per 100 ml., were 23·4 ± 0·7 and 98·5 ± 0·8 mg. respectively. F. A. R.

Organic

Estimation of Weak Acids by Direct Titration in a Mixed Solvent. S. R. Palit (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 246–251)—The method depends upon the fact that all salts of monobasic weak organic acids containing the group COONa are highly soluble in a glycol or a mixture of a glycol with some solvent for hydrocarbons. Such mixtures may be referred to as G–H mixtures, where G stands for the glycol and H for any solvent for hydrocarbons (*e.g.*, hydrocarbons themselves, alcohols, chlorinated hydrocarbons, etc.). The solns. thus obtained can be titrated directly with hydrochloric acid or perchloric acid dissolved in the same solvent mixture, the end point being determined either potentiometrically or by means of indicators. The method can likewise be used with a few weak inorganic acids the salts of which are soluble in the aforementioned solvents and can also be applied to determine excess of base present in a neutral salt, since no free base is produced by hydrolysis. Thus by a double titration first with phenolphthalein or cresol red as indicator and then with methyl orange or methyl red both the free base and the combined base can be determined. Since weak acids are far less dissociated in non-aqueous solvents (*e.g.*, alcohol) than in water, their sodium salts act as bases towards indicators. However, most are only slightly soluble in such solvents and the end-point is not sharp because the colour change or the *p*H change extends over a wide range. The solvent medium now proposed provides high solubility and a sharp end-point. Almost any G–H mixture can be used but, in making the choice, attention has been paid to sharp end-point, high solvent power, low viscosity, low volatility, freedom from toxicity and commercial availability. Of the three commercially available glycols, ethylene glycol is slightly preferable to propylene glycol and to diethylene glycol but the advantage is not decisive. From the many solvents for hydrocarbons *iso*propyl alcohol has been chosen as co-solvent with ethylene and propylene glycols as best meeting all requirements. In extreme instances (*e.g.*, with sodium stearate) *iso*propyl alcohol does not confer sufficient hydrocarbon dissolving power and hence more powerful solvents, such as butyl or amyl alcohol, chloroform, dioxane, etc., may be used. The proportion of *iso*propyl alcohol that can be used as co-solvent with glycol ranges from 15 to 70% by volume, but a 1 : 1 mixture (by vol.) of ethylene or propylene glycols with *iso*propyl alcohol has been used as a standard solvent and although a 20% proportion of the latter solvent is slightly better, the low viscosity of the 1 : 1 mixture is an advantage. Although hydrochloric acid and perchloric acid give equally good results the latter has the advantage that the perchlorate formed is much more soluble than the chloride and does not cause haziness in the soln. during titration.

Potentiometric titrations were made satisfactorily with a Beckman glass electrode. The readings on the dial of the *p*H meter indicate, of course, only apparent *p*H values because the scale of acidity has not been thermodynamically established for these solvents and because the value of the potential at the liquid junction between the solvent and the sat. potassium chloride soln. surrounding the reference electrode is not known. Nevertheless the *p*H changes and the behaviour of the indicators are nearly in the same range as in an aqueous medium in the weakly acid region. In the strongly acid region the apparent *p*H is much lower. In a 0·1 *N* acid soln. it is negative, and hence, except as a means of determining the end-point, these values have no significance.

The same titration can be made with suitable indicators, 0·2 to 1·0 g. of the salt being dissolved in 10 to 15 ml. of the solvent mixture, and titrated with 0·18 *N* (or stronger) perchloric acid in presence of 3 to 5 drops of 0·05% alcoholic indicator soln. Blank titrations are not necessary even with the commercial solvents, but chloroform may contain free acid and should be washed with water and dried before use as co-solvent with the glycol. Owing to uncertainties in the significance of *p*H measurements in organic solvents, the choice of indicator has to be made by trial and error. Either methyl red or methyl orange may be used, the latter giving a sharper and the former a brighter end-point. Methyl red was generally found preferable.

Any sodium salts containing the group XOONa, where X stands for any negative element, are highly soluble in G–H mixtures and can be titrated accurately in such media. Among the inorganic salts having this structure are metaborates, aluminates, nitrites, nitronates, hypophosphites, hyposulphites, sulphinates and chlorites. There are also a number of monobasic weak inorganic acids the salts of which are sufficiently soluble in G–H mixtures to allow titration by this method. Among these are borates, silicates and arsenates. All the alkali-metal borates are highly soluble and can easily be estimated. Dissolve the salt in the G–H solvent, and titrate with glycolic alkali to the phenolphthalein or cresol red end-point. Then titrate with glycolic perchloric acid to the methyl red end-point. This gives the total boric acid provided no other weak acid is present in the system. The method can be applied also to the titration of weak bases such as aniline, alkaloids, *p*-toluidine, naphthylamine, pyridine and quinoline. Strychnine and brucine give sharp end-points, aniline, quinoline and *p*-toluidine fairly sharp end-points, but pyridine and naphthylamine give less satisfactory end-points unless the soln. is titrated quickly. With the bases better colour changes occurred when chloroform was used as co-solvent. A. O. J.

Determination of 1:2-Propylene Glycol in Ethylene Glycol. R. C. Reinke and E. N. Luce (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 244–245)—The basis of the method is the micro application by Shupe (*J. Assoc. Off. Agr. Chem.*, 1943, **26**, 249) of the procedure of Nicolet and Shinn (*J. Amer. Chem. Soc.*, 1941, **63**, 1456), who determined methyl pentose in presence of pentose by oxidation with periodate and separation of aldehydes by aeration. The oxidation of glycerol by the periodate method of Malaprade (*Compt. rend.*, 1928, **186**, 382; ANALYST, 1928, **53**, 299) and Fleury and Fatome (*J. pharm. Chim.*, 1935, **21**, 247) and its adaptation to glycols by Denigè (private communication) may be expressed by the equations

$$C_2H_4(OH)_2 + HIO_4 = 2CH_2O + HIO_3 + H_2O$$

$$CH_3CHOHCH_2OH + HIO_4 = CH_2O + CH_3CHO + HIO_3 + H_2O,$$

the ethylene glycol yielding 2 mol. of formaldehyde and the 1:2-propylene glycol 1 mol. each of formaldehyde and acetaldehyde. The aldehydes are separated by blowing them through a sat. soln. of sodium bicarbonate containing a definite amount of glycine, the formaldehyde being thus removed, and the acetaldehyde is then determined by the sulphite procedure.

The apparatus consists of a series of 4 test tubes connected for passage of gas through their contents. The first tube (200 × 29 mm.) is fitted with a 3-hole rubber stopper carrying a small separating funnel through which the sample aliquot and periodate solns. are added. The funnel serves also as an inlet tube for the carbon dioxide stream. A glass tube of wide bore also inserted in the stopper of the first tube is divided above the stopper by a piece of rubber tubing and serves as a reservoir and an inlet for the sodium bicarbonate powder. A pinch clamp on the rubber tubing prevents loss of gas when the sodium bicarbonate is added. The other tubes in the series measure 150 × 25 mm. To determine total glycols place an aliquot of not more than 30 ml. containing 15 to 90 mg. of glycols (as ethylene glycol) in a 125-ml. Erlenmeyer flask, add 15 ml. of 0·1 *M* periodic acid (10·7 g. of sodium metaperiodate treated with 200 ml. of water and 100 ml. of *N* sulphuric acid and finally made up to 500 ml.). Allow the mixture to stand for 15 min. then add 30 ml. of sat. sodium bicarbonate soln. to render the liquid approximately neutral and add exactly 50 ml. of 0·1 *N* sodium arsenite and finally 1 ml. of 10% potassium iodide soln. and an excess of solid sodium bicarbonate. Titrate the mixture with 0·1 *N* iodine to the yellow end-point, which is easily detected with practice. Make a blank determination by treating 15 ml. of 0·1 *M* periodic acid in the same manner. The amount of 0·1 *N* iodine used, corrected by the blank determination, is equivalent to the periodic acid used to oxidise the ethylene glycol and 1 : 2-propylene glycol. The total glycol (%) as ethylene glycol is given by ml. of 0·1 *N* iodine used × 0·003102 × 100/sample wt. This result, less the amount of 1 : 2-propylene glycol (*infra*) multiplied by 31/38, is the amount of ethylene glycol (%) in the sample. Glycerol, if present, must be determined and accounted for since it is oxidised by periodic acid to formaldehyde and formic acid. The formic acid produced may be titrated.

To determine 1 : 2-propylene glycol dilute a sample of the proper wt. to a suitable vol. so that a 10- to 20-ml. aliquot will contain not more than 10 mg. as 1 : 2-propylene glycol. Pipette an aliquot into the largest test tube of the series and stopper the tube after adding water (if necessary) to make the final volume 25 ml. In the second tube place enough glycine to leave a 10% excess over the amount required to remove the formaldehyde, avoiding too large an excess which may remove some of the acetaldehyde. If the ethylene glycol content is unknown make a trial determination first and calculate the amount of glycine from the result. To the second tube add enough sat. sodium bicarbonate soln. to make the final volume 10 ml. In the third and fourth tubes place 1 ml. of 5% sodium bisulphite soln. and 15 ml. of water. Place 15 ml. of 0·1 *M* periodic acid in the separating funnel and connect the carbon dioxide line through a flow meter. Allow the acid to run into the reaction tube, mix the soln. gently for 15 min. by passing in a small stream of carbon dioxide, and meanwhile place 4 g. of solid sodium bicarbonate in the wide-bore glass tube. At the end of the 15-min. period remove the pinch clamp and tap-in the sodium bicarbonate, replace the clamp and pass in carbon dioxide at the rate of 1·5 litres per min. for 1 hr. Transfer the contents of the third and fourth tubes into a 250-ml. Erlenmeyer flask with the aid of a wash bottle, add 5 ml. of starch soln. and run in 0·1 *N* iodine from a burette until a blue colour persists, avoiding addition of a large amount at any one time. Discharge the blue colour by adding a drop of 5% sodium bisulphite soln. and after 5 min. add 0·02 *N* iodine until the blue end-point is attained. Now add 10 ml. of sat. sodium bicarbonate soln. and again titrate to the blue colour with 0·02 *N* iodine. Before taking the final end-point add 10 ml. of borax - carbonate buffer prepared by dissolving 4 g. of borax (decahydrate) and 5 g. of anhydrous sodium carbonate in 100 ml. of water. Record the total vol. of 0·02 *N* iodine used after the excess of sodium bisulphite had been removed by the first addition of 0·02 *N* iodine and calculate the % by wt. of 1 : 2-propylene glycol by means of the formula

ml. of 0·02 *N* iodine × 0·00076
× aliquot factor × 100/sample wt.

In the lower ranges of 1 : 2-propylene glycol concentration good recovery was attained, but in the higher ranges the results tended to be slightly low owing to interaction between the glycine and a very small amount of acetaldehyde. Substances containing adjacent hydroxyl groups or an amino group adjacent to a hydroxyl group interfere with the determination. A. O. J.

Simultaneous Determination of Ethylene and 1:2-Propylene Glycols. B. Warshowsky and P. J. Elving (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 253–254)—Ethylene glycol and 1 : 2-propylene glycol can be determined simultaneously by periodate oxidation to formaldehyde and acetaldehyde which are determined polarographically after distillation. The method is applicable to the analysis of mixtures of formaldehyde and acetaldehyde as well as to the determination of other substances that form these aldehydes after treatment. The principal limitation of the method is that there must not be formed any other volatile substances polarographically reducible under the same conditions as the aldehydes. The acetaldehyde formed is a measure of the 1:2-propylene glycol content of the sample. The ethylene glycol can then be determined by deducting the formaldehyde produced by oxidation of the propylene glycol from the total amount of formaldehyde found in the oxidised mixture.

Pipette the aqueous soln. of the glycol mixture containing about 5 to 20 mg. of each of the glycols into a 100-ml. Kjeldahl flask, add about 3 ml. of the periodic acid soln. (approximately 0·5 *N*, prepared by dissolving 11 g. of periodic acid in water and diluting to 100 ml.) and add enough water to bring the volume to about 60 ml. Insert a few glass beads to prevent bumping. Connect the Kjeldahl flask in an upright position with the distillation apparatus using a deep receiver (*e.g.*, a Pyrex test tube, 45 × 190 mm.) containing 75 ml. of water to absorb aldehydes and immersing the tip of the condenser to a depth of several cm. To minimise loss of acetaldehyde immerse the receiver in ice water during the distillation. Heat the contents of the flask gently at first and distil at the rate of 3 to 4 ml. per min. until about 5 ml. remain in the flask. Near the end of the distillation lower the receiver so that the end of the condenser no

longer dips below the surface of the liquid. Finally rinse the end of the condenser with water.

Transfer the distillate quantitatively into a 250-ml. flask, taking care not to exceed a volume of 225 ml. Immediately before polarographic analysis add 25 ml. of *N* lithium hydroxide soln. in 0·1 *N* lithium chloride soln. to the distillate and dilute the mixture to 250 ml. The resulting soln. has a concn. of 0·1 *N* lithium hydroxide in 0·01 *N* lithium chloride, and in this manner condensation of the aldehydes in presence of alkali is reduced to a minimum. Rinse the polarographic cell and electrodes several times with the soln. to be analysed. Place a sample of the soln. in the cell and allow it to attain constant temp. After a definite time has elapsed from the moment of adding the supporting electrolyte soln. read the galvanometer deflections at applied voltages of −1·890, −1·610 and −1·400 volts. The height of the acetaldehyde wave is the difference in the galvanometer reading between the first and second points and the height of the formaldehyde wave is the difference between the second and third points. These wave heights are then compared with the values obtained from a 250-ml. soln. prepared from standard aldehyde solns. containing approximately the same concns. of the aldehydes as the sample soln.

The weight of 1:2-propylene glycol in the sample (W_p) is

$$1{\cdot}727 \times V \times H_a \times C_s/H_s$$

where C_s is the concn. of acetaldehyde (mg. per ml.) in the standard soln., V the vol. (ml.) of standard acetaldehyde soln. taken, H_a the acetaldehyde wave height from oxidation of the glycol mixture and H_s the acetaldehyde wave height of the standard. The % by weight of 1:2-propylene glycol in the sample is then $100W_p/S$ where S is the wt. of the sample in mg.

The wt. of ethylene glycol in the sample (W_e) is

$$(1{\cdot}033 \times V \times H_f \times C'_s/H'_s) - 0{\cdot}408W_p$$

where C'_s is the concn. (mg. per ml.) of formaldehyde in the standard soln., V the vol. (ml.) of standard formaldehyde soln. taken, H_f the formaldehyde wave height from oxidation of the glycol mixture and H'_s the formaldehyde wave height of the standard. The % of ethylene glycol in the sample is then $100W_e/S$.

The values obtained at three different temperatures indicate that within the range of 20° to 30° C. the height of the formaldehyde wave increases approximately 6·5% for each 1° C. rise of temp. The acetaldehyde wave height, however, increases only about 1·5 to 2·0% per degree. The data obtained show that under the conditions used there is a linear relation between the height of the wave and the corresponding aldehyde content of the soln. resulting from oxidation of the glycol mixture.

Material capable of being oxidised by periodic acid to form acetaldehyde or formaldehyde must be absent. This includes such substances as α-amino acids, alcohols, hydroxyamino acids and polyalcohols (glucose and other sugars). Monohydroxyalcohols in general do not affect the determination.

A. O. J.

Determination of Reducing Sugars. Mathematical Expression of Reducing Action in the Lane and Eynon and Ferricyanide Methods. F. W. Zerban, W. J. Hughes and C. A. Nygren (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 64–65)—The values in the Lane-Eynon tables (*J. Soc. Chem. Ind.*, 1932, **42**, 32T) for the various reducing sugars agree closely with equations of the form $\log y = \log b - m \log x$, in which y is the volume of sugar soln. required (from 15 to 50 ml.), x is the concentration of the solution and b and m are constants for the same sugar and the same volume of Fehling's solution used. Values of b and m for the various sugars are given and those for invert sugar in presence of 0, 1, 5, 10 and 25 g. of sucrose per 100 ml. Inserting these values in the equation above, the authors calculated values of y from 15 to 50 ml. and found agreement with the table values usually to within 0·05 ml.

Equations of the same form were found to apply to determinations of invert sugar in presence of 0, 1, 3, 5 and 10 g. of sucrose per 100 ml. by the alkaline ferricyanide volumetric method. The reagent used contained 56·00 g. each of potassium ferricyanide and potassium hydroxide per litre; 10 ml. were taken and the Lane-Eynon technique was followed except that 20 ml. of water was added before the addition of the sugar solution. The results, for quantities of invert sugar from 400 to 160 mg. per 100 ml., alone and in presence of sucrose as above, are tabulated. The effect of sucrose is considerable, as in the Lane-Eynon method. The precision was found to be not quite so high as that of the latter method; when the titre lay between 35 and 50 ml. differences of 0·2–0·3 ml. often occurred. It is therefore considered advisable to keep the titre between 15 and 35 ml.

Inorganic

Routine Analysis of Manganese Bronze. E. K. Babson and W. W. Johnson (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 292–293)—The method is claimed to give a complete analysis of manganese bronze with sufficient accuracy for control and inspection purposes in approx. 5 hr. The sample is dissolved in perchloric and nitric acids and a pptn. with hydrogen sulphide separates copper, lead and tin from iron, aluminium, manganese, nickel and zinc. Manganese is determined on a separate sample by existing methods (Scott, "*Standard Methods of Chemical Analysis*," 5th Ed., Vol. II, p. 1358, New York, D. Van Nostrand Co., 1939) and zinc is determined by difference.

Method—Weigh 1·000 g. of the bronze into a 400-ml. beaker, dissolve in 4 ml. of conc. nitric acid and 6 ml. of perchloric acid (70%), cover, and heat until fumes of perchloric acid are evolved for several min. Cool, dilute to 200 ml. with hot water and pass hydrogen sulphide for 20 min. Add paper pulp, coagulate the ppt. by heating the soln. to boiling, filter (Whatman No. 30) and wash the ppt. thoroughly with hot water.

Tin—Wrap the sulphide ppt. and filter paper in another filter paper, place in a clean porcelain crucible and ignite at 500° C. Cool, transfer the residue to a 150-ml. beaker and heat 10 ml. of conc. nitric acid in the crucible for several min. Pour the acid into the beaker and wash the crucible with 10 ml. of water, adding the washings to the acid. Heat until the black copper oxide dissolves, dilute to 50 ml. with hot water, add paper pulp and keep the soln. nearly at the boiling point for 30 min. Filter through a Whatman No. 42 paper containing paper pulp. Wash the ppt. 3 times, alternately with hot water and hot diluted nitric acid (1+4). Burn off at 500° C. in a weighed crucible, ignite at 900° C., cool and find the weight of SnO_2.

Copper and Lead—Dilute the filtrate from the tin ppt. to 200 ml. and add 2 ml. of diluted sulphuric acid (1+1) and a small amount of urea or sulphamic acid. Electrolyse to deposit the copper on a weighed

gauze cathode and the lead as PbO_2 on the weighed rotating gauze anode. With customary electrodes the process takes about 60 min. with a current of 2·5 amp. Reweigh the electrodes.

Iron—To the filtrate from the sulphide pptn. add a few glass beads to prevent bumping and boil the soln. vigorously for 30 min. to expel hydrogen sulphide. Cool in ice water, add 10 ml. of diluted sulphuric acid (1+1) and titrate with 0·05 *N* potassium permanganate until a faint pink colour persists for 10 to 15 sec.

Aluminium—Add 10 g. of ammonium chloride to the titrated iron soln., and add ammonia soln. (sp.gr. 0·90) until just alkaline to methyl red. Add paper pulp, boil, add 3 drops of ammonia soln. and leave for 5 min. Filter (Whatman No. 31) and wash 3 times with hot 10% ammonium nitrate soln. which has been made just ammoniacal to methyl red. Reserve the filtrate for the nickel determination. Dissolve the ppt. into the pptn. beaker with hot diluted hydrochloric acid (1+1). Add 2 g. of ammonium chloride to the soln. and reppt. the hydroxides as above. Filter, wash, burn off the paper at 500° C. in a weighed porcelain crucible, ignite at 900° C., cool and find the weight of $Fe_2O_3 + Al_2O_3$. Calculate the amount of aluminium.

Nickel—Add to the filtrate from the first ammonia pptn. 15 ml. of 1% alcoholic dimethylglyoxime soln. Warm until the ppt. coagulates, filter through a Whatman No. 41 paper, and wash 8 to 10 times with hot water. Wrap the filter in moist ashless filter paper, ignite in a weighed, covered porcelain crucible, first at 500° C. and then at 800° C., cool and weigh the NiO.

The precision and accuracy of the results of analyses of standard samples are good; possibly fortuitous compensation of errors leads to better results than might be expected. Presence of silicon in the sample appears to lead to high values for tin and aluminium. L. A. D.

Gas Analysis

Determination of Methyl Chloride in Air. J. L. Franklin, E. L. Gunn and R. L. Martin (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 314–316)—The method is claimed to be quick, sufficiently accurate for safety control purposes, safe to use in presence of gaseous hydrocarbons, specific for chlorine compounds and to use portable equipment.

Apparatus (patent applied for)—The apparatus, shown in the diagrams, is mainly of glass with joints made with surgical rubber tubing. The electrodes are made from ¼″ diam. spectrographic carbon rods and the flame arrester G consists of a 1″ roll of 100 mesh copper gauze in a glass tube. (The text indicates that the smaller hole in electrode C is

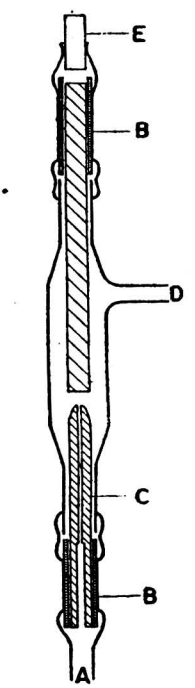

Figure 1. Reaction Chamber

A. Inlet
B. Copper collar
C. Hollow carbon electrode, 1/8 and 1/32 inch diameter
D. Outlet
E. Glass plug

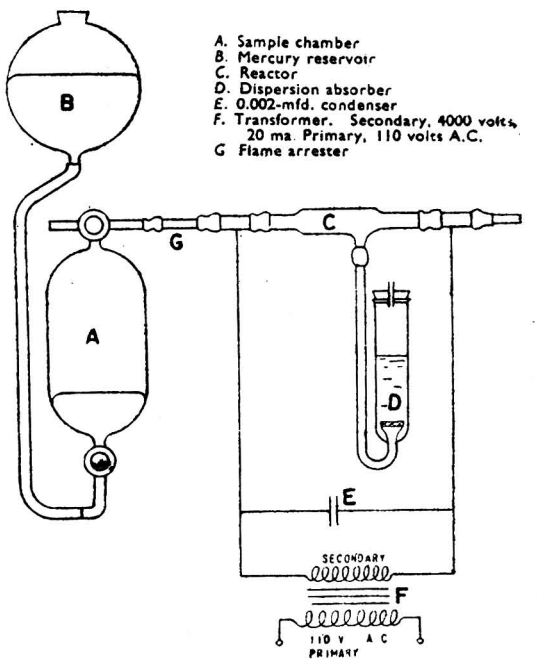

Figure 2. Complete Assembly

1/16″ diam.). The sintered glass disc at D (Fig. 2) is of such porosity that the gas flow recommended below requires a pressure of 4 to 6 cm. of mercury.

Reagents—Sodium arsenite (approx. 0·1 *N*): dissolve 4 g. of sodium hydroxide and 4·9 g. of pure arsenic trioxide in 50 ml. of water and dilute to 1 litre. Chloride soln. (0·1 mg. of chlorine per ml.): dissolve 1·648 g. of sodium chloride in 1 litre of water, and dilute 100 ml. to 1 litre. Silver nitrate (approx. *N*): 17 g. in 100 ml. of water.

Method—Draw the sample, at atmospheric pressure, into A (Fig. 2). A volume of 250 to 300 ml. is sufficient if the methyl chloride concn. exceeds 200 p.p.m. Place 15 ml. of sodium arsenite soln. in absorber D, run a steady spark between the electrodes and pass the sample through the reaction chamber (275 ml. in 7 to 8 min.). Flush with 100-ml. of chlorine-free air. Pour the soln., and three 5-ml. water rinses, from the absorber into a 50-ml. beaker. Add a drop of phenolphthalein soln., acidify with conc. nitric acid and add 3 drops in excess. Transfer to a 50-ml. Nessler cylinder, dilute to the mark and add 3 drops of *N* silver nitrate. Mix thoroughly. Compare the turbidity with that of standards made by adding standard chloride soln. to acidified 15-ml. portions of sodium arsenite soln. and proceeding as above.

$$\text{P.p.m. of methyl chloride} = \frac{n \times 1{,}000{,}000}{13{\cdot}67 \times V}$$

where n = ml. of standard chloride soln. and V = ml. of sample. This equation assumes a temperature of 27° C. and includes a factor of 0·95 to compensate for systematic error. A few determinations where sulphur compounds were also present suggested that no interference occurs if the combustion is complete. L. A. D.

Physical Methods, Apparatus, etc.

Amperometric Titration of Chloride, Bromide and Iodide and of Halide Mixtures, using the Rotating Platinum Electrode. H. A. Laitinen, W. P. Jennings and T. D. Parks (2 Papers, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 355–358 and 358–359)—The titration of halides may be followed by measuring the diffusion current of silver ions and the end-point determined by plotting the current against the volume of silver soln. used. If a rotating platinum electrode is used the sensitivity is good as the effective thickness of the diffusion layer is reduced and a steady state is quickly achieved. In titrating halides the potential of the rotating electrode must be sufficiently negative to plate out silver ions but not negative enough to reduce dissolved oxygen. The saturated calomel electrode (S.C.E.) happens to have its potential in the required range so that the apparatus consists simply of the rotating electrode connected through a galvanometer (about 0·01 microamp. per mm.) to a S.C.E. The rotating electrode consists of a piece of 18-gauge platinum wire sealed into the end of a glass tube so that 5 to 10 mm. project. The tube is bent at right angles 2 cm. from the lower end and an internal wire is connected to the platinum by a small amount of mercury. The wire is connected to the galvanometer by means of a mercury cup; a sliding contact or a contact through the spindle bearings is not satisfactory. The galvanometer is fitted with an Ayrton shunt. The S.C.E. is of large area to avoid polarisation. In typical titrations the whole cell has a resistance of the order of 1,500 to 2,000 ohms. When it is necessary to titrate in ammoniacal soln. a more negative potential is required and the S.C.E. is replaced by a mercury - mercuric iodide - potassium iodide cell (Kolthoff and Harris, *Id.*, 1946, **18**, 161).

Chloride—Good results are obtained with 0·01 *N* chloride in presence of 0·01 to 0·4% of gelatin, 0·08 *N* to 3·2 *N* nitric acid and 0·08 *N* to 9·2 *N* sulphuric acid. With solns. weaker than 0·005 *N* (100 ml. of soln., 0·8 *N* in nitric acid and containing 0·1% of gelatin) addition of an equal volume of acetone reduces the solubility of silver chloride, and with 0·0001 *N* soln. the error is about 10%. If the acetone concentration is 75% the error is reduced to 3%.

Bromide—Gelatin was added but was later found to be unnecessary. The results tend to be slightly low in 0·8 *N* nitric acid, and acetone is advantageous with dilute solns. In aqueous medium 0·001 *N* bromide can be titrated; in 50% acetone 0·0001 *N* bromide gave a 3% error. Ammonia (0·01 *N*) does not affect the bromide end-point with bromide concn. 0·001 *N*.

Iodide—As well as being satisfactorily titrated in acid soln. iodide may be titrated in presence of 0·1 *N* to 0·3 *N* ammonia, which prevents chloride and bromide from interfering.

Mixtures—All three halides can be titrated in one soln. as follows. Titrate the iodide in presence of ammonia, add acid and titrate the bromide, and then add gelatin and titrate the chloride. The chloride titration relies on the observation that silver chloride particles depolarise the cathode in absence of gelatin, while silver bromide and iodide do not.

It is suggested that in all titrations the lowest convenient galvanometer sensitivity be used. The papers include details of the bibliographical and theoretical background of the work and many results of titrations under various conditions. L. A. D.

Conductometric Titrations with Organic Reagents. Determination of Copper and Iron. J. F. Corwin and H. V. Moyer (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 302–304)—The apparatus consists of a conductivity cell of about 200 ml. capacity immersed in a thermostat bath and a simple A.C. Wheatstone bridge. The bridge is energised by an electrically maintained tuning fork, and a 7-watt amplifier, coupled to the bridge by a transformer and feeding crystal earphones, is used as the detector. The titration curves consist of two practically straight lines of different slope intersecting at the end-point. The curves may be drawn, or the end-point calculated by taking each part of the curve as having the form $y=mx+c$ where x is the volume of titrant and y is the slide-wire ratio $(1000-a)/a$. The two values each of m and c are found and the equations are solved simultaneously for x. No correction of the slide-wire ratio for the added volume of titrant is made unless the volume exceeds 10 ml.

Copper—Cupferron soln. (30 g. in 500 ml. of water) is used as titrant.

$$Cu^{\cdot\cdot} + 2C_6H_5N(NO)ONH_4 \rightarrow Cu[C_6H_5N(NO)O]_2 + 2NH_4^{\cdot}$$

The release of ammonium ions causes the conductivity to increase before the end-point; then combination of excess cupferron with hydrogen ions causes a fall in conductivity. *Method*—Dissolve 4 g. samples of brass or bronze in nitric acid, add 4 ml. of sulphuric acid, evaporate to fuming, cool and dilute to 1,000 ml. Transfer 50 ml. to the cell, dilute to 200 ml. and titrate, adding the cupferron soln. 2 ml. at a time; and measure the conductivity in terms of the slide-wire ratio after each increment. Standardise the titrant against pure copper. When

the sample contains more than 5% of tin the soln. may be filtered before evaporating with sulphuric acid. Lead, zinc, nickel and cobalt do not interfere but iron reacts with cupferron and causes high results. The titrant is stable for 3 days if kept in a dark bottle. In longer periods an appreciable amount of nitrobenzene separates and may be removed by filtering the soln. *p*-Acetophenetide (0·3–0·4 g. per litre) has been suggested as a preservative for cupferron solns.

Iron—Sulphosalicylic acid (15% soln.) or its ammonium salt (10% soln., prepared by adding the solid acid to ammonia soln. until acid to methyl red) may be used to titrate ferric iron solns. The iron solns. are prepared by the usual methods and oxidised by means of bromine or hydrogen peroxide.

L. A. D.

Preparation of Silica Gel for Chromatography. R. A. Harris and A. N. Wick (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 276)—Silica gel suitable for partition chromatography can be prepared by the following method; the material was shown to be satisfactory for the isolation of pure penicillin. Mix 34 l. of sodium silicate, sp.gr. 1·38—1·40, with 10 l. of water and add 10 *N* hydrochloric acid very slowly (17 litres in 2½–3 hours) with vigorous stirring until the mixture has a *p*H of 2·0–2·8. When about 4 litres of the acid have been added a very thick gummy mass is formed and at this point the addition of acid is stopped and the mass is thoroughly broken up with a heavy wooden paddle. More acid is then added dropwise with stirring until a thin suspension results, when the rate of addition of the acid can be increased. Digest the suspension at 25° C. with continuous stirring for 2 hours and then filter on a large stoneware filter; break up the cake of silica gel to facilitate filtration. Leave the silica gel in 0·2 *N* hydrochloric acid, as recommended by Gordon, Martin & Synge (*Biochem. J.*, 1943, **37**, 79; ANALYST, 1943, **68**, 283), for 2 days to increase the buffer-adsorbing titre (ageing"), and then suspend the gel in tap water, filter, wash until free from acid, dry at 200° C. for 12 hours and grind to a particle size of 50 to 150 mesh. Wash the ground silica gel with distilled water until free from chloride and dry in shallow pans at 250° C. for 24–48 hours. Transfer the final product, which should weigh about 15 kg., to dry bottles whilst still hot. Silica gel prepared without ageing adsorbs 85–100% of its weight of water without becoming lumpy or moist, whilst the aged material adsorbs 20–40% more. The unaged material was found to be quite satisfactory for purifying penicillin.

F. A. R.

A Rapid-filling Capillary Polarimeter Tube. D. Smith and S. A. Ehrhardt (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 81)—Measurement of the optical rotation of very small quantities of liquid when only polarisation tubes of the usual bore are available has hitherto been relatively inexact owing to the use of a very short tube or to the necessity for dilution. The use of tubes of normal length but capillary bore involves difficulties in filling, owing to air locks; these difficulties are usually overcome by introducing the liquid from a long thin dropper which will extend to the bottom of the tube and can be raised as the tube fills, but the fragility of the dropper is a serious disadvantage. The reading of liquids in tubes of very small bore is difficult owing to the "halo" caused by light scattered from the inner walls. The authors eliminate this, at the expense of a small reduction in the diameter of the field, by mounting a diaphragm in the threaded end of the tube nearest the polariser, the hole of the diaphragm being of such size that it subtends at the observer's eye a smaller angle than does the end of the capillary bore nearest the analyser.

For small quantities of liquid the authors use tubes of normal length and bore but provide for them capillary glass tubes which can be inserted in them as liners when necessary. Several of these liners, of different bores, may be provided for the same polarimeter tube; they should be about 0·5 mm. shorter than the polarimeter tube, their external diameter should give a snug sliding fit inside the ordinary tube (clearance about 0·01 mm.), and they should be optically polished on both ends. Filling is effected easily, rapidly and safely by putting the small necessary amount of the liquid into the ordinary tube and then slowly lowering the capillary liner into it. Water-jacketed tubes without tubulures may be similarly converted to capillary tubes, but owing to the extra thickness of tube wall temperature equilibrium will be attained much more slowly than usual.

Reviews

INTRODUCTION TO BIOCHEMISTRY. By W. R. FEARON, M.A., Sc.D., M.B. Third Edition. Pp. x + 568. London: William Heinemann, Ltd. 1946. Price 21s. net.

There is such a thing as being taken too strictly at one's word. It was said in a review of the first edition of Professor Fearon's "Introduction" (ANALYST, 1934, **59**, 372) that it was "one of the best summaries of modern biochemistry for the use of analytical and other practising chemists" and of the second edition (ANALYST, 1940, **65**, 387) that there was "no book more suitable to the analyst—or any non-biochemist—who wishes to revive his knowledge (or create it) of modern biochemistry, and none more handy for the biochemist as a working book of reference, in which respect it sets a very high standard for completeness, lucidity and accuracy." These observations were neither more nor less than expressions of the reviewer's honest opinions. But their effect on his library shelves has been unintended, even though it might have been foreseen, were not the reviewer a modest man incapable of really believing that any poor words of his could lead to action, let alone criminal action.

For it has to be admitted that neither the first nor the second edition of Professor Fearon's book is any longer on his shelves. Some analyst, perhaps,—but no, possibly a biochemist,

or, more likely, one of those non-biochemists—has permanently borrowed one or both of them; whether this be absentmindedness or larceny, the result is the same. There is no possibility of indulging in the reviewer's favourite pastime of comparing Edition 3 with Edition 2, for nothing remains of Edition 2, save the fleeting words, apparently this time all too cogent, of its review.

He must therefore consider the Third Edition of "An Introduction to Biochemistry" *ab ovo*, or *ab initio*—at any rate, on its merits. And how well it stands up to such consideration. It is divided into two main parts: Part I is entitled "Elements and Inorganic Compounds" and has four chapters on "The Subject Matter of Biochemistry," "Biological Elements," "Inorganic Compounds" and "Solutions and Colloidal Systems," totalling 80 pages. Part II, under the general title of "Organic Biochemistry," occupies a further 460 pages odd, and includes 21 chapters. Two useful Appendixes, one on food materials and their composition and chief characteristics, and one giving the commoner reagents employed in biochemistry (including a useful list of "H-ion indicators") as well as a table of abbreviations and equivalents, then lead to a Subject Index of 13 pages.

It is naturally to Part II that the analyst and biochemist will most frequently turn. It is the bulk of the book, because (as was said in an earlier review) of "the unfairness of nature, which insists on being much more organic than inorganic," in spite of Professor Fearon's declared intention, according to that review, of approaching "the living organism . . . along the less worn path of *inorganic biochemistry*." Apparently Nature has won—she generally does—for the Preface to the First Edition has vanished, and along with it the author's claim to an unexpected approach.

All the same, the book has a freshness of outlook that does not appear to fade with the passing of years and editions. The first chapter itself is a model of philosophic breadth and scientific conciseness. Metaphysics the author neatly sidesteps, with a hint that he has Whitehead's authority for so doing, and remarks in passing that "To a disembodied and detached observer, a living organism is only a form in which carbon is collected, stored and oxidised." Perhaps the word "slowly" should be added to this apothegm, for it is surely the delicate gradation of the oxidative steps in carbohydrate catabolism, with the consequent liberation of energy in utilisable but non-pyrogenic amounts, that characterises the energetics of life.

It will be seen that Fearon tempts even the hardened reviewer to reflection, if not to philosophy. The book abounds with passages having that effect, even among the highly condensed factual matter that constitutes its Part II. Read his remarks about oxygen (p. 262), about energy exchange (p. 393), about the uterine cycle (pp. 494/5) and many others. In order to read them, you will need to acquire the book. Do so. Buy it for yourself, and don't borrow mine.

A. L. BACHARACH

CANNED FOODS: AN INTRODUCTION TO THEIR MICROBIOLOGY. By J. G. BAUMGARTNER. Second Edition. Pp. xi + 239. London: J. & A. Churchill, Ltd. 1946. Price 12s. 6d.

That the second edition of this book has followed so soon after the first (1943) is substantial evidence of its value to technologists in the canning industry, for whose benefit it was primarily written. The general layout has not been altered to any great extent, but the incorporation of additional material has increased the number of pages from 157 to 239. Four new chapters have been included, dealing with true fungi, containers, the microbiology of sound canned foods, and the examination of raw materials, plant and miscellaneous methods. The other chapters, which deal most ably with the scientific principles of food preservation, spoilage, public health aspects, and the laboratory examination of canned foods, have been carefully revised and extended.

All the various aspects of the microbiology of canned foods are dealt with clearly and concisely and the useful list of references given at the end of each chapter indicates that the author has supplemented his wide, practical knowledge by a very thorough study of the original literature.

The second edition of this little book, clearly printed on good white paper, is strongly recommended to technologists in the canning industry and to others who are interested directly or indirectly in the wholesomeness of canned food.

F. HIRST

PLASTICS—SCIENTIFIC AND TECHNOLOGICAL. By H. R. FLECK, M.Sc., F.R.I.C. Second Edition. Pp. xlii + 361. London: Temple Press, Ltd. 1946. Price 30s.

In the new edition of this book, which was first published in 1944, the author follows his original plan of providing a review of a very wide field. Not only is an account given of the technology of the various plastics, including thermo-plastic and thermo-setting resins, fibres, adhesives and synthetic elastomers, but the chemistry of their formation as well as the properties of ancillary materials and the finished products are also discussed. As an indication of the wide scope of the book there may be mentioned the short description of the application of cation- and anion-exchange resins to water treatment, a subject omitted from most comparable publications. The table of properties of 100 plasticisers is an illustration of the detail provided in some sections of the subject.

The second edition of *Plastics—Scientific and Technological* has 36 pages more than the first, but the two chapters containing analytical methods have no share in this expansion: there is actually a reduction in Chapter XIV, "The Chemical Analysis of Raw Materials," due to improved presentation of the material. It is to be regretted that the author did not take the opportunity to revise Chapter XV, "The Chemical, Physical and Electrical Testing of Plastics." This subject is still receiving attention from investigators, notably the chemists. In particular, Nechamkin's scheme for the identification of plastics, which is given in full, serves as a very useful preliminary guide, but it is neither so complete nor so certain as the systematic procedure of T. P. Gladstone Shaw (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 541) which is not mentioned. Although 36 pages are devoted to Chapter VI, "Synthetic Elastomers or Rubber-like Plastics," these materials are not considered at all in the chapters on testing and analysis.

The silicone plastics are in production in America and are attracting a great deal of technological attention, so that the newcomer to the subject ought not be misled by the overcautious statement on p. 90 that "These resins, although at present mainly of theoretical interest, have recently become of considerable importance owing to the *possibility* of their technical application." It must be admitted regretfully, however, that manufacture in this country still awaits the future.

G. H. WYATT

ORGANIC REAGENTS FOR ORGANIC ANALYSIS. By the Staff of the Research Laboratory of Hopkin & Williams, Ltd. London: Hopkin & Williams, Ltd. Pp. 172. Price 5s. 6d.

This book is an excellent companion to *"Organic Reagents for Metals,"* a book from the same laboratory and one by now familiar to most chemists. That volume described the use of organic reagents for the detection and estimation of metals, whereas the main function of this new one is the identification of organic compounds by the preparation of suitable derivatives which may be subsequently distinguished by their melting points.

It is assumed that the operator has determined or knows the group of organic compounds (*e.g.*, amino or acidic compound, alkaloid and so forth) to which the substance to be identified belongs so that he can proceed immediately to the preparation of suitable derivatives.

The book is divided into three sections. The first is devoted to a general survey of the many different organic reagents described in the literature for the preparation of derivatives of organic compounds for purposes of identification. From the numerous reagents described for identification purposes the authors select those which in their experience have proved to be most suitable. This selection is based upon, among other considerations, simplicity and speed with which derivatives can be prepared, accessibility and stability of reagent, and convenient melting point range and sufficient difference between the melting points of closely related compounds to enable identification to be made.

In the second section the reagents selected in Section I receive individual treatment. The characteristics and properties of the reagents are described and finally experimental details are given for the preparation of derivatives.

In Section 3 the melting points of the derivatives of the more common organic compounds with the selected reagents described in Section 2 are given in tabular form.

This book summarises all the organic reagents which have been described from time to time and which were scattered about the literature and frequently difficult to find. One is amazed at the number of organic compounds that have been suggested for identification purposes; in each instance full references to the original papers are given.

It is to be hoped that subsequent editions of this book will appear and that besides new reagents an increasing number of compounds will be given in the melting point tables, thus adding considerably to the value of the book.

J. HUBERT HAMENCE

MODERN CHEMISTRY: SOME SKETCHES OF ITS HISTORICAL DEVELOPMENT. By A. J. BERRY, M.A. Pp. $x + 240$. London: The Cambridge University Press. 1946. Price 10s. 6d.

In chemistry, as in every other science, there is need, at times, for the student to lay aside his studies in order to survey the ground already covered; for it is only in this way that his knowledge can be consolidated and further progress made, since in chemistry, as in other spheres of human activity, the best guide to progress is a knowledge of the past. At considerable cost in time and trouble every chemist can make this survey for himself; but the ability to do so with literary skill and acumen is not given to everyone. Fortunately there have never been wanting a few men of wide knowledge, critical ability and command of words to undertake the task. Amongst these the author of this, the most recent of such surveys, should take a high place.

The book consists of a collection of historical essays on chemical theory, written with the emphasis on the theories themselves rather than on the personalities of those who have contributed to their making. No attempt is made to deal with all the branches of chemistry, but within the limits of the chosen subjects the treatment, from the earliest conceptions to the modern position, is thorough and complete. The separate essays treat of: the atomic theory; electrochemistry; stereo-chemistry; radioactivity; elements, isotopes and atomic numbers; experimental studies on gases; some problems of solution; and some essential features of chemical change; followed by a retrospect containing some apposite remarks on the progress made by general chemical theory through its association with physical and biological thought; and also on the impetus given to analytical chemistry by physical methods and organic reagents.

The text is written in a lucid style that connects the older with the newer aspects of chemistry in a way that makes for easy reading without overburdening the story with too much detail; it is free from errors and misprints, but there are infelicities on pages 148 and 222. Reference is facilitated by a synoptical list of contents, a separate index to names and subjects, and a selected bibliography following each chapter.

The book is, for these days, well produced in clear type, not too closely spaced. It should have a wide appeal. To the student it will be essential; to the teacher, useful; and to any chemist who may find himself losing sight of the chemical tree because of his interest in one particular branch, it will bring interest, instruction and pleasure. F. L. OKELL

PHYSICAL METHODS GROUP

THE Annual General Meeting of the Physical Methods Group will be held in the rooms of the Chemical Society, Burlington House, W.1, at 6.0 p.m., on Tuesday, November 26th, 1946.

The business meeting will be followed at 6.30 p.m. by a meeting open to non-members, when three short papers on Polarographic Analysis will be read.

POLAROGRAPHIC DISCUSSION PANEL

The Committee of the Physical Methods Group have decided to form a Polarographic Discussion Panel. The object of the Panel will be to hold and sponsor informal discussions on Polarographic Analysis. It is intended that the Panel should be inaugurated at the forthcoming Annual General Meeting of the Group. Members of the Physical Methods Group who wish to become members of the Polarographic Discussion Panel are asked to notify the Honorary Secretary of the Group, Dr. J. E. Page, at Glaxo Laboratories Ltd., Greenford, Middlesex.

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