THE ANALYST

A Monthly Publication dealing with all branches of Analytical Chemistry: the Journal of the Society of Public Analysts and Other Analytical Chemists

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Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 78 Price 6s. 6d.
Subscription Rate, inclusive of Abstracts C, 80/- per annuni, Post Free
No. 927, Pages 333-388 June, 1953

An Humble Address
To Her Most Excellent Majesty
Queen Elizabeth II

May it please Your Majesty,

We, the President, Council and Members of the Society of Public Analysts and Other Analytical Chemists, Your Majesty's loyal and dutiful subjects

Present our humble duty to Your Majesty on the occasion of Your Majesty's Coronation and tender our congratulations to You with loyal pride.

Charged as we are with the development of Analytical Chemistry, we gratefully recognize the gracious interest taken by Your Majesty in the advancement of Chemistry and in its application to the welfare of Your People,

We humbly assure Your Majesty of our deep and faithful allegiance and we give expression to the ardent hope that Your Majesty may long be spared to reign over Your devoted and happy People.

Signed and Sealed on behalf of the Society of
PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

D. W. Kent-Jones — President

Herbert Hamence — Honorary Treasurer

Kenneth Williams — Honorary Secretary

2nd June, 1953

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, April 1st, 1953, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. This was the first meeting under the Chairmanship of the new President, Dr. D. W. Kent-Jones, F.R.I.C., and about 170 members and visitors were present.

The subject of the meeting was "The Determination of Small Amounts of Lead in Foods and Biological Materials" and the following papers were presented and discussed: "A Reversion Method for the Absorptiometric Determination of Traces of Lead with Dithizone," by H. M. Irving, M.A., D.Phil., F.R.I.C., L.R.A.M., and E. J. Butler, B.A., B.Sc., D.Phil., A.R.I.C.; "Preparation of Samples of Foodstuffs and Biological Materials for the Determination of Lead," by R. F. Milton, B.Sc., Ph.D., F.R.I.C., (presented by K. J. Jarrett, B.Sc., A.R.I.C.); "Sample Preparation for Determination of Lead in Foodstuffs," by D. A. Elvidge, B.Sc., and D. C. Garratt, B.Sc., Ph.D., F.R.I.C.

NEW MEMBERS

Frank Banyard; William Robert Charles Crimmin, B.Sc. (Wales); Charles Brian Dennis; Edward Frank Hancock, Ph.C.; Alan Frederick Hulme, A.R.I.C.; Louis Francis McCallum, F.R.I.C.; Joel Alfred Henry Totterdell Rosewarne, B.Sc. (Lond.), A.R.I.C.; Arthur George Sansome, B.Sc. (Lond.), A.R.I.C.; Frederick Clarence Saville, A.R.I.C.

DEATH

WE regret to record the death of

Walter Thorp.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held at 7.15 p.m. on Friday, April 10th, 1953, in the George Hotel, George Street, Edinburgh, 2.

A lecture on "Modern Methods of Analysis in the Training of the Student" was given by Miss Christina C. Miller, Ph.D., D.Sc., F.R.S.E., F.H.-W.C.

PHYSICAL METHODS GROUP

THE Fortieth Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, April 14th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. This meeting was organised by the Polarographic Discussion Panel. The Chairman of the Group, Dr. J. Haslam, F.R.I.C., opened the meeting and invited Mr. G. W. C. Milner, B.Sc., F.R.I.C., A.Inst.P., Honorary Secretary of the Panel, to occupy the Chair for the rest of the meeting.

The following papers on "Polarography" were presented and discussed: "The Polarographic Determination of Fluoride," by B. J. MacNulty, B.Sc., Ph.D., F.R.I.C., G. F. Reynolds, B.Sc., A.R.I.C., and E. A. Terry; "The Amperometric Titration of Zinc and its Application to the Determination of Zinc in Lubricating Oils," by D. Pickles, B.Sc., A.R.I.C., and C. C. Washbrook, A.R.I.C.; "A Tentative Method for the Determination of Calcium by Means of the Polarograph," by Mrs. Bertha Lamb, B.Sc.

The Precipitate Error in the Determination of Sugar Polarisations

By J. G. N. GASKIN and G. C. HANDS

The final volumes, nominally 100 ml, of sugar solutions defecated by wet or dry methods have been theoretically compared.

In both methods of defecation it has been shown that the final volume of 100 ml is in the first place diminished by the liquid volume of the obscuring matter (a term defined in the text) and that this figure is further modified in opposite directions according as wet or dry defecation is used.

In making this theoretical comparison it is assumed that minimum amounts of lead salt or solution of similar basicity are used in the defecation and that no changes of volume occur at the moment of precipitation. The assumptions have been tested and experiments are described, including some with a special type of flask designed for use in the determination of any volume changes during the precipitation.

Finally the value of a "standard volume" has been proposed and the method by which this can be most nearly achieved in practice is indicated.

At the tenth session, in 1949, of the International Commission for Uniform Methods of Sugar Analysis, the British National Committee recommended that the continued use of the wet method for the clarification of raw-sugar solutions was justified. Both American and Australian interests disagreed with this and advocated the official use of dry lead coupled with the use of a correcting factor to be applied to wet-lead clarification. The implication that the figure found by the dry-lead method is necessarily correct is not acceptable to the sugar chemists in this country, and this difference of opinion remains to be resolved. Before this is possible, additional information is required on a number of points, and it has been our purpose to provide this information and derive therefrom a theoretical approach to the problem of precipitation.

Polarisation figures found by the dry-lead method are known to be lower than similar figures found by wet methods, but the value of this difference has not been satisfactorily determined, and advocacy of the merits of either figure has been based on rather vague assessments of errors associated with such factors as the volume of the precipitate, the "salt effect" of the excess of lead, the varying basicity of lead solutions, the amount of lead used, and so on. Further, the increasing discrepancy between the two figures with decreasing purity of the raw sugar has been assigned wholly to errors involved in the wet method, which may not be justifiable. It would be true to say that the appeal of the dry-lead method rests on the unproved assumption first claimed by Horne[1] that "whereas in the usual procedure the error is proportional to the volume of the total precipitate, in this dry defecation the error is only proportional to the difference in volume of acetic acid and the precipitated radicals involved." Hence it is apparent that the following information is required—

1. The changes in polarisation produced by the use of lead sub-acetate solutions of different basicities.
2. The value of the critical minimum amount of lead defecant.
3. The value of the volume changes, if any, that occur at the moment of precipitation.
4. The value of any other volume changes occurring during the defecation process.

Experimental

The information required under headings 1 and 2 above was obtained as follows. About 5 lb of Cuban raw sugar having a polarisation of about 97° was thoroughly mixed and bottled. A series of standard solutions of this sugar was clarified by the wet method, two different lead solutions, each of known basicity and density, being used. One of the lead solutions was the stock basic lead acetate used in this laboratory; it had a density of 1·25 and a ratio of basic lead to total lead of 0·332. The other was a solution of Horne's dry lead, which had a density of 1·25 and a ratio of basic lead to total lead of 0·434, the latter figure approximately corresponding to the basicity of Horne's dry lead.

The defecated solutions were made up to 100 ml and filtered, and the polarisations of the clarified solutions were determined; all of these operations were carried out at 20° C. The full results of these experiments are shown in Table I.

The evaluation of the volume changes on precipitation of the obscuring matter involved bringing together in a calibrated flask, but without mixing, solutions of the sugar and defecant, together with water to make the total up to a known volume, then mixing by some suitable

TABLE I

CLARIFICATION OF STANDARD SOLUTIONS OF CUBAN SUGAR

Volume of basic lead solution used, ml	Basic Lead A		Basic Lead B		Differences, A − B
	Character of filtration	Average polarisation	Character of filtration	Average polarisation	
0·1	Poor	Unreadable	Poor	Unreadable	—
0·2	Poor	Unreadable	Poor	Unreadable	—
0·3	Poor	Unreadable	Slow	96·91*	—
0·4	Slow	96·83	Moderate	96·86*	− 0·03
0·5	Moderate	97·01	Moderate	96·85	+ 0·16
0·6	Fairly rapid	97·01	Good	96·88	+ 0·13
0·7	Fairly rapid	97·02	Good	96·94	+ 0·08
0·8	Good	97·01	Good	96·95	+ 0·06
0·9	Good	97·05	Good	96·96	+ 0·09
1·0	Good	97·09	Good	97·03	+ 0·06
1·2	Good	97·10	Good	96·98	+ 0·12
1·4	Good	97·15	Good	97·01	+ 0·14
1·6	Good	97·12	Good	97·04	+ 0·08
1·8	Good	97·04	Good	97·06	− 0·02
2·0	Good	97·11	Good	97·05	+ 0·06
2·2	Good	97·11	Good	97·11	0·00
2·4	Good	97·11	Good	97·10	− 0·01

* The polarsiation of these solutions was difficult to determine.

Defecants—Basic Lead A: sp.gr. 1·25; ratio of basic lead to total lead 0·332.
Basic Lead B: sp.gr. 1·25; ratio of basic lead to total lead 0·434.

method and finally re-measuring the total volume, all measurements being made at 20° C. For this purpose a special flask of approximately 100 ml capacity was designed. About 10 cm of the stem of this flask consisted of tubing with an internal diameter of 3·5 mm, and the capacity of the flask to a point about midway along this stem was accurately determined. The mixing experiment was carried out as follows.

TABLE II

VOLUME CHANGES ON PRECIPITATION OF OBSCURING MATTER

Particulars of flask—
Internal diameter of stem, 3·5 mm.
Capacity to mark, 98·448 ml.
1 linear millimeter on stem equivalent to 0·0096 ml.
Defecant used, Basic Lead B (see Table I).

Sugar used	Defecant added, ml	Average depression of meniscus with defecant, mm	Average depression of meniscus without defecant, mm	Difference between depressions, mm	Volume represented by difference between depressions, ml
Cuban (Pol. 96.95) ..	0·7	6·1	6·4 (≡0·061 ml)	0·3	0·003
Mauritius (Pol. 98.70)	0·3	8·0	9·4 (≡0·090 ml)	1·4	0·014
Barbados (Pol. 95.33)	0·9	7·5	8·6 (≡0·082 ml)	1·1	0·011

The above experiments were carried out on a sugar solution containing, before dilution, 26 g in 53 ml. Similar experiments carried out on a sugar solution containing, before dilution, 26 g in 90 ml, showed no measurable depression of the meniscus level when finally mixed.

A standard weight, 26 g (or the equivalent proportion when the calibrated volume of the flask differed from 100 ml), of Cuban sugar was dissolved in the minimum amount of water and transferred to the flask, the flow into the flask being facilitated by inserting into the stem of the flask a finely drawn glass tube through which air could escape or be gently withdrawn. A layer of water was floated on top of this sugar solution, and then the requisite amount of basic lead acetate solution, and the flask and contents, without mixing, were placed in a thermostatically controlled bath at 20° C. The flask was finally filled to the mark at 20° C, after which the solutions were mixed by rotating the flask by means of a mechanical stirrer. When it was certain that mixing was complete, the flask was returned to the 20° C bath and, when the temperature of the contents of the flask had again reached 20° C, the position of the liquid level was measured.

This experiment was repeated four times, both with and without defecant, on the Cuban sugar described above, and later with sugar from Mauritius and Barbados. The complete results are shown in Table II.

In further experiments, the polarisations of these three types of sugar were determined, both dry and wet defecants being used and the stage at which the solutions were mixed being varied. These results can be seen in Table III.

TABLE III

DEPENDENCE OF POLARISATION ON TYPE OF DEFECANT AND STAGE AT WHICH SOLUTIONS WERE MIXED

Sugar	Basic Lead B (see Table I)			Horne's Dry Lead		
	Volume used, ml	Polarisation of solution mixed before making up to volume	Polarisation of solution not mixed before making up to volume	Weight used, g	Polarisation of solution mixed before making up to volume	Polarisation of solution not mixed before making up to volume
Mauritius ..	0·4	98·68	98·77	0·132	98·60	98·74
Cuban ..	0·7	97·05	97·15	0·231	96·95	97·00
Barbados ..	0·9	95·29	95·38	0·306	95·15	95·24

RESULTS

THE EFFECT OF VARYING THE BASICITY OF THE LEAD DEFECANT (TABLE I)—

It is evident that solutions of Cuban sugar clarified with the lead solution of lower basicity have for the most part higher polarisations than the solutions clarified with the lead solution of higher basicity. This difference is apparent almost from the first readable solution and is maintained until more than 1·6 ml of lead solution have been added, after which the two defecants produce almost identical figures. A statistical analysis of all the figures shows—

(*i*) That the differences observed are significant, *i.e.*, they cannot be explained by random error.

(*ii*) That the degree of correlation between the two sets of figures is such as to make it reasonably certain that a variation in some factor common to both series of reading is the cause of the differences.

It appears that this variable is in fact the different basicity of the two lead solutions. The disappearance of the differences in the results after the addition of more than 1·6 ml of lead is susceptible to a number of interpretations and needs further investigation.

It can also be seen that the amount of lead solution required to defecate a sugar solution adequately can be determined within narrow limits, that this amount is generally less than 1 ml, and that it is smaller for the solution of higher basicity. Similar results have been found for sugars from Mauritius and Barbados. Hence it is possible, for accurate comparisons of the two methods, to select comparable minimum amounts of lead sub-acetate solutions, such that most of the lead will be used in the precipitation of the obscuring matter and therefore the "salt effect" of the excess of lead on the polarisation will be reduced to a minimum and made strictly comparable. Similar considerations can equally well be extended to dry-lead defecations.

VOLUME CHANGES ON PRECIPITATION (TABLE II)—

The control experiment in which no lead defecant was used revealed a measurable diminution in volume when a known volume of concentrated sugar solution was diluted with a volume of water. This diminution, amounting to about 0·1 ml, is of the same order as the differences under investigation, and it is of the utmost importance that it should be avoided in all determinations of sugar polarisation. Fortunately this can be done by mixing after dilution to 90 ml, when further dilution to 100 ml produces no measurable diminution of volume. The effects of this error on the recorded polarisations are shown in Table III to be significant for the three different types of sugar examined. Because of this effect it was necessary to ensure that the volumes of the concentrated sugar solution were the same in all experiments.

When this contraction is allowed for, it will be seen from the figures in Table II that any change in total volume of the sugar solution caused by precipitation of the obscuring matter is very small (of the order of 0·01 ml), and hence it can be stated that the solid volume of the precipitate is not sensibly different from the liquid volume of the obscuring matter (defined below) together with the liquid volume of that part of the lead salt involved in the precipitation.

THEORETICAL CONCENTRATION OF A DEFECATED SUGAR SOLUTION

The view that one method of determining polarisation is more accurate than another implies the existence of some standard to which both are referred. The nature of this standard can only be determined by a study of the generally accepted methods for determining polarisations. These are essentially the dissolution of a standard weight of sugar, 26 g, in water, the adjustment of the volume of this solution to 100 ml and the subsequent "testing by the polariscope." If the accuracies of the initial weighing, of making up to volume and of the final reading are assumed, the value of the figure indicated by the polariscope is obviously dependent on the concentration of optically active substances in the final clear solution. It is this concentration for which some standard value is required, and it is variations in this concentration, caused by the need to clarify the sugar solution, that give rise to the differences of opinion mentioned in the first paragraph of this paper and that are now being considered.

The solution made by dissolving raw sugar in water is, with few exceptions, optically opaque and needs clarification before the polarisation value can be determined. This clarification is achieved by the addition of a suitable defecant, usually some form of basic lead acetate, and filtration to remove the precipitated matter. In the wet method this clarification is performed before dilution to 100 ml by the addition of a solution of the lead salt, and in the dry method clarification is performed after dilution by the addition of dry lead salt. In both methods the separation and removal of the precipitate may modify the concentration of the optically active substances remaining in the clear solution and also disturb their optical activity. The exact nature of the precipated material and the extent of the optical disturbance are both irrelevant to the comparison to be made, provided that all precautions are taken to ensure that the same precipitate and effects are produced by both methods; that is to say, that minimum amounts of lead salt or solution, of similar basicity, are used. It has already been shown that there is no sensible change in total volume caused by the separation of the precipitate (Table II). The theoretical approach to this problem can be made as follows.

A solution of a particular raw sugar, of volume 100 ml, can be regarded as consisting of three parts, of volumes V_s, V_o, V_w, their total volume being—

$$V_s + V_o + V_w \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where V_s is the liquid volume (*i.e.*, the volume occupied by the molecules of the dissolved material) of the optically active substances, mostly sugars that would not be removed by clarification,

V_o is the liquid volume of the material that would be removed were the solution clarified, and

V_w is the volume of water necessary to make 100 ml.

The nature of V_o is such that this solution cannot be examined in the polarimeter, and to do this requires the elimination of V_o. Were this possible without addition to the solution, the remaining liquid would have a volume—

$$V_s + V_w \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

which is numerically equal to $100 - V_o$.

It will be shown that this volume, $V_s + V_w$, with additives or subtractives, is common, for a given sugar, to both methods of defecation under consideration; further, it contains all the optically active substances not removed by clarification. It is, therefore, a suitable standard volume with which to compare the two defecated solutions.

DEFECATION BY THE WET METHOD—

The practical elimination of V_o is not achieved by eliminating V_o alone, but by adding something to it and removing the precipitate so produced. The additive is usually basic lead acetate, which may be added as a solution before making up to volume (wet method), or as the dry salt after making up to volume (dry method). In either method the liquid volume of the lead salt has to be considered, and this can be represented by two parts, an electrically positive part, V_{L^+}, and an electrically negative part, V_{L^-}, and the amount added can be so adjusted that V_{L^+} will just precipitate V_o. Hence, for the wet method, the 100 ml of solution before the precipitation will consists of—

$$V_s + V_o + V_{L^+} + V_{L^-} + V_{w_1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where V_s, V_o, V_{L^+}, V_{L^-} have the meanings already assigned, and V_{w_1} is the volume of water necessary to bring the total volume to 100 ml.

On precipitation, V_o and V_{L^+} become associated as a solid and, as already shown, this association is without significant change of volume. On filtration they will be eliminated, and the remaining clear solution will have the volume—

$$V_s + V_{L^-} + V_{w_1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

The expressions (1) and (3) both represent a total volume of 100 ml, and we can therefore derive from them a value for V_{w_1}, which is—

$$V_w - V_{L^-} - V_{L^+}$$

and, substituting this value in expression (4), we have as the final volume after wet-lead defecation—

$$V_s + V_w - V_{L^+} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

Hence, in the wet method, the final volume as compared with the standard volume is diminished by an amount equal to the liquid volume of the electrically positive part of the lead salt added, and therefore the polarisation of this solution will be greater than that of the standard sugar solution.

DEFECATION BY THE DRY METHOD—

A similar treatment can be applied to the dry method. The solution before the addition of the dry salt will have a volume—

$$V_s + V_o + V_w \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

To this is added an amount of dry lead such that the electrically positive part will just precipitate V_o. Hence the volume becomes—

$$V_s + V_o + V_w + V_{L^+} + V_{L^-} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

After precipitation and filtration, V_o and V_{L^+} are associated as a solid without change in volume and the remaining volume is—

$$V_s + V_w + V_{L^-} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

Hence, in the dry method of defecation, the final volume as compared with the standard volume is increased by an amount equal to the liquid volume of the electrically negative part of the lead salt added, and therefore the polarisation of this solution will be less than that of the standard.

DEFINITION OF POLARISATION—

The numerical values of the volumes shown in expressions (2), (5) and (7) are—

(2)	$100 - V_0$	the standard volume,
(5)	$100 - V_0 - V_{L+}$	wet defecation,
(7)	$100 - V_0 + V_{L-}$	dry defecation.

On reference to the standard volume, the amounts and directions of the errors are apparent. The necessity for a definition of polarisation that indicates the final volume to be attained is obvious. The temptation to use 100 ml for this volume must, however, be avoided as unrealistic. Polarisation is an empirical term universally associated with the quality of raw sugar and the determination of its value equally universally involves some form of defecation. It would be manifestly unreal to define it with reference to a pure substance dissolved in a volume that, in practice, is unattainable by the wet method and only accidentally attainable by the dry method. For example, defecation by the wet method will never produce a final volume greater than $100 - V_0 - V_{L+}$, although it may always be equal to this value whatever the amount of lead added. By the dry method, the final volume can be between $100 - V_0$ and 100, can be equal to 100, or can exceed 100, depending on the respective values of V_0 and V_{L-} for the sugar under examination; and the final volume will increase with increasing amounts of added lead. To choose between the two methods is difficult; the dry method gives a volume nearer to the academically desired 100 ml, but this volume is more susceptible to error due to an excess of lead; the wet method avoids this error, but gives a volume slightly more remote from 100 ml. It would appear, therefore, that at present the standard volume after clarification should have the numerical value $100 - V_0$, and this will be most nearly achieved in practice by taking the mean of the figures found by the dry and wet methods of clarification.

CONCLUSIONS

Under critical conditions it has been shown that differences in the basicity of the lead salt used in the defecation of sugar solutions produce differences in the polarisations subsequently determined.

There is a critical value for the amount of a defecant that will just clarify a given sugar solution.

Small volume changes, which occur when a concentrated sugar solution is diluted, are sufficient to affect polarisation figures and must be avoided in practice.

A theoretical comparison of the concentration of optically active substances in the solutions obtained after wet and dry defecation shows both to be different, in opposite directions, from the concentration of a suggested standard solution. The magnitude of the difference is a function of the amount of defecant added and not of the total volume of the precipitate.

Within the limits of existing knowledge, it is suggested that in the critical determination of the polarisation of a raw sugar the most satisfactory value is that given by the mean value of the figures found by wet and dry defecation methods, provided that these determinations have been performed with corresponding minimum amounts of lead salt or solution of similar basicity.

The authors wish to thank Mr. A. H. Rheinlander, M.Sc., F.R.I.C., for criticism and suggestions, Mr. J. W. Stiles for practical assistance, and the Government Chemist, Dr. G. M. Bennett, C.B., F.R.S., for permission to publish this paper.

REFERENCE

1. Horne, W. D., *J. Amer. Chem. Soc.*, 1904, **26**, 186.

THE LABORATORY
GOVERNMENT CHEMIST'S DEPARTMENT
CUSTOM HOUSE
LONDON, E.C.3

November 24th, 1952

The Determination of the Amount and Composition of Free Phenols in Phenol - Formaldehyde and Cresol - Formaldehyde Resins and Moulding Powders

By J. HASLAM, S. M. A. WHETTEM and G. NEWLANDS

A method has been evolved for the determination of total free phenols in phenol - formaldehyde, cresol - formaldehyde and phenol - cresol - formaldehyde moulding powders. In addition, tests have been devised whereby the ratio of free phenol to free cresol in the total free phenols contained in a moulding powder can be determined.

It has also been shown that the ratio of *m*-cresol to *p*-cresol can be determined in the total free cresols present in a cresol - formaldehyde moulding powder prepared from *m*-cresol and *p*-cresol only. It has not been possible to extend the principles of this method to the corresponding combination of *o*-cresol and *m*-cresol or to that of *o*-cresol and *p*-cresol.

Phenol - formaldehyde resins are made by the condensation of phenol or cresols or mixtures of phenol and cresols with formaldehyde. These resins invariably contain a certain amount of the free phenols from which they are prepared, and it has been found that the amount of free phenols in the resins affects the properties of the moulding powders prepared from them. It is important, therefore, to know the amounts of these free phenols present in the resins, and to have as much information as possible about their composition.

It is also possible by the same methods to get a useful indication of the proportions of phenolic and cresylic resins used in the manufacture of a moulding powder of unknown composition. This can be done by determining the free phenol and cresols in moulding powders of known composition, and then finding the relationship between the free phenols and cresols remaining in the powders and the proportions of phenolic and cresylic resins used in the manufacture of the powders.

The method that we have used for some years for the isolation of the total free phenols from a resin or moulding powder is based on dissolving the sample in aqueous sodium hydroxide, precipitating the resin by neutralisation of the solution to pH 4·5, filtering off the resin (and fillers where moulding powders are concerned) and steam distilling the phenols in the filtrate. The phenols in the steam distillate are then determined by modifications of the Koppeschaar[1] bromination method.

For simple phenol - formaldehyde resins, this is all that need be done. But for resins prepared from a mixture of phenol and cresols, however, it is often desirable to know the proportions of phenol and cresols in the free phenols. It has not been possible to resolve chemically all mixtures of phenol and *o*-, *m*- and *p*-cresols when they occur in low concentrations in aqueous solution, although there is little doubt that modern methods of chromatographic testing are of considerable value for this resolution.

This, however, is not so important as it might appear. It is well known that, when a resin is made from a mixture of phenol and commercial cresylic acid containing all three isomers, then, because of the very high reactivity of *m*-cresol with formaldehyde, no free *m*-cresol is likely to be present in the free phenols remaining in the resin. These free phenols will therefore consist of phenol, *p*-cresol (the least reactive) and possibly a small amount of *o*-cresol. The proportion of phenol and cresols in this important combination can be determined. The method described in full later is based on—

(*i*) A knowledge of the behaviour o phenol and *p*-cresol towards bromination by potassium bromide - potassium bromate mixture under the conditions of the test.

(*ii*) Application of Chapin's method[2] for the determination of phenol in the presence of certain other phenols to an aliquot of the steam distillate, the bromination value of which is known. Chapin's method is based on the knowledge that, under certain conditions, Millon's reagent gives a red colour with phenol but not with certain other phenols.

Another combination that has been resolved is that of free *m*-cresol and *p*-cresol in resins prepared solely from *m*- and *p*-cresols. In this method too a knowledge of the bromination value of the steam distillate is the first requirement. The determination then depends on the difference in colour intensity of the nitrosamine solutions prepared from the two isomers by a modification of the method of Savitt, Goldberg and Othmer.[3]

BEHAVIOUR OF PHENOL AND CRESOLS ON BROMINATION—

It has been shown by Sprung[4] that when phenols are brominated by Koppeschaar's method, *i.e.*, with aqueous bromine liberated by acid from potassium bromide - potassium bromate mixture, some phenols behave normally, whereas others behave abnormally as regards the amount of bromine they absorb. Phenol and the cresols, for instance, are said to react according to the following scheme—

	Bromine atoms combining with 1 molecule of the phenol
Phenol	2·98 (theory 3·0)
m-Cresol	2·98 (theory 3·0)
o-Cresol	2·20 (theory 2·0)
p-Cresol	2·27 (theory 2·0)

Sprung concludes from these and other results that the presence of one primary alkyl group in the *ortho* or *para* position to the hydroxyl group of a phenol results in the absorption of from 0·1 to 0·3 molecule of bromine beyond that required by the simple theory of *ortho* and *para* substitution.

As our interest lay, in the first place, in the determination of free phenol in phenol - formaldehyde resins and free cresols (known to be mainly *p*-cresol) in cresol - formaldehyde resins, known amounts of phenol and *p*-cresol in the concentrations found in our steam distillate were brominated and titrated by our usual procedure. The factors found for these phenols were as follows—

1 ml of 0·1 *N* sodium thiosulphate ≡ 0·00157 g of phenol
1 ml of 0·1 *N* sodium thiosulphate ≡ 0·00236 g of *p*-cresol

The figures are in good agreement with those found by Sprung, showing nearly theoretical bromination for phenol and 2·29 atoms of bromine combining with 1 molecule for *p*-cresol.

BEHAVIOUR OF PHENOL AND CRESOLS TOWARDS MILLON'S REAGENT—

Chapin found that if he mixed solutions of phenols (4 mg in 6 ml of water) with 5 ml of Millon's reagent and heated the mixtures in a bath of boiling water for 30 minutes, the red colour produced with phenol became much intensified, whereas the red colours first produced with the cresols soon gave place to various shades of yellow. He found that, after acidification with a definite amount of nitric acid, the solutions underwent no appreciable change in colour for many hours. The colours with phenol and the cresols are as follows—

	Colour of solution
Phenol	Deep red
o-Cresol	Faintly orange
m-Cresol	Strong yellow
p-Cresol	Greenish yellow

To develop this test into a quantitative method for determining phenol in the presence of other phenols, he describes three different procedures. The procedure that we have found applicable to the steam distillates obtained from resins is that described in "Standard Methods for Testing Tar and its Products."[2]

APPLICATION TO THE DETERMINATION OF FREE PHENOLS AND CRESOLS IN RESINS AND MOULDING POWDERS—

For resins and moulding powders that are known to have been prepared from phenol only or cresols only, it is necessary first to isolate the free phenols by steam distillation of the filtrate from the filtration of the resin precipitated at pH 4·5 from a sodium hydroxide solution of the sample. It is then only necessary to brominate an aliquot of the steam distillate and to calculate the amount of free phenol or free cresols from the bromine absorbed in terms of 0·1 *N* potassium bromide - potassium bromate.

For mixed phenol - cresol resins, the free phenols are isolated and an aliquot of the steam distillate is brominated as before. A note is made of the bromine absorbed in terms of 0·1 *N* potassium bromide - potassium bromate. A volume of the steam distillate calculated to give a titration of 3·00 ml of 0·1 *N* potassium bromide - potassium bromate is taken and diluted to 100 ml with water. The phenol is determined in this solution with Millon's reagent by the procedure described in "Standard Methods of Testing Tar and its Products."[2] By dividing the weight in grams of phenol found in this solution by 0·00157, the number of millilitres of 0·1 *N* potassium bromide - potassium bromate required to account for the phenol can be found. Then 3·00 ml minus this volume will be the proportion of the 0·1 *N* potassium bromide - potassium bromate titre accounted for by the cresols in this solution. From these results the proportions of the bromide - bromate titre due to phenol and to cresols in the original steam distillate can be calculated and, by using the respective factors for phenol and cresol, the amounts of free phenol and cresols in the sample can be found. The method is described in full below.

Method for determining total free phenols

Sample—

The size of the sample to be taken depends on the amount of free phenol expected to be present. For resins containing from 10 to 20 per cent. of free phenols, 2 g is sufficient. For moulding powders, 5 g is generally sufficient, but sometimes it may be necessary to take as much as 10 g of sample.

Procedure—

Place the weighed sample in a 500-ml beaker and add 50 to 200 ml of 10 per cent. sodium hydroxide (according to the size of sample). Boil the contents of the beaker for about 10 minutes to bring everything except the fillers, if present, into solution. Cool the solution and dilute to about 200 ml.

Adjust the pH of the solution to 4·5 with 20 per cent. sulphuric acid at first, and then with *N* sulphuric acid, using B.D.H. "4·5" indicator externally.

Filter off the precipitated resin and wash it well with cold water. Transfer the filtrate and washings, which contain the free phenols, to a 500-ml flask, dilute to the mark and shake thoroughly.

Transfer 250 ml of this solution to a steam distillation apparatus. Steam distil until 350 to 400 ml of distillate have been collected in a 500-ml calibrated flask. Dilute the distillate to the mark with water and mix well. Transfer 250 ml to a 500-ml "Iodine" flask for bromination.

Add 50 ml of an approximately 0·1 *N* solution of potassium bromide - potassium bromate mixture and 10 ml of 20 per cent. v/v sulphuric acid. Stopper the flask and put a few millilitres of 10 per cent. w/v aqueous potassium iodide solution into the trough formed by the stopper and the mouth of the flask so that no bromine escapes. Carry out a blank determination simultaneously and allow both flasks to stand in the dark for 1 hour. Ease the stoppers and allow the potassium iodide to run into the flasks and add a further 15 ml of 10 per cent. potassium iodide solution to each, taking the usual precautions to prevent loss of bromine. Titrate the liberated iodine with 0·1 *N* sodium thiosulphate solution until the iodine colour has been discharged to a pale straw colour, add a few millilitres of chloroform to dissolve the very voluminous precipitate of tri-bromophenol, as this absorbs appreciable quantities of iodine, and complete the titration after adding starch as indicator. The amount of phenol (or cresol) is calculated from the difference between the blank and sample titres.

1 ml of 0·1 *N* sodium thiosulphate ≡ 0·00157 g of phenol
1 ml of 0·1 *N* sodium thiosulphate ≡ 0·00236 g of cresol

Method for determining the ratio of free phenol to free cresol

Sample—

From the steam distillate prepared as described above, an amount is taken that would give a titre of 3·0 ml of 0·1 *N* potassium bromide - potassium bromate. This amount of distillate is measured from a burette into a 100-ml calibrated flask, diluted to the mark with water and mixed thoroughly. This constitutes the sample solution for the method to be described.

REAGENTS—

Nitric acid, diluted—Prepare this by bubbling air through pure concentrated nitric acid until the acid is colourless and then dilute one volume of the acid with four volumes of water.

Millon's reagent—This reagent is prepared as follows. Measure 2 ml of mercury from a burette into a 100-ml conical flask and add 20 ml of pure concentrated nitric acid. Hasten the resulting reaction by occasional shaking. When all action has ceased (after about 15 minutes), add 35 ml of water. If any separation of basic mercury nitrate occurs, add diluted nitric acid reagent drop by drop until the solution clears. Add 10 per cent. w/v aqueous sodium hydroxide drop by drop with thorough mixing until the curdy precipitate that forms no longer redissolves but just produces a slight permanent turbidity. Add 5 ml of dilute nitric acid reagent and thoroughly mix the contents of the flask. Millon's reagent so prepared will remain stable for 2 days.

Standard phenol solution—Prepare a stock 1 per cent. w/v solution of phenol in water. Prepare the standard phenol solution from this on the day it is used by taking 2·5 ml of stock solution and making up to 100 ml with water, so that the solution contains exactly 0·025 g of phenol per 100 ml.

Formaldehyde solution—Dilute 2 ml of 40 per cent. v/v formaldehyde solution with water to make 100 ml of solution.

PROCEDURE—

Measure 5 ml of the sample solution into each of two 6 × 1-inch test tubes and mark them A and B, respectively. Into each of two similar tubes measure 5 ml of the standard phenol solution and mark them C and D. Measure from a burette 5 ml of Millon's reagent into each of the four tubes and mix thoroughly. Place the tubes in a water-bath maintained at 100° C for 30 minutes. Remove the tubes and cool them immediately in a bath of cold water for 10 minutes. Remove them from the cold water and add 5 ml of dilute nitric acid reagent to each tube and gently shake to mix the contents. To tubes A and C add 3 ml of the formaldehyde solution. Dilute the contents of the four tubes to 25 ml with water (the tubes should be previously marked with a file scratch at the 25-ml level), shake them thoroughly and set them aside overnight.

The contents of tubes A and C will then be found to be yellow because of the bleaching action of the formaldehyde; these are used as blanks in the colorimetric procedure that follows.

Measure 20 ml of the contents of tubes C and D by means of a pipette into separate 100-ml calibrated flasks and mark these C and D, respectively. Add 5 ml of diluted nitric acid reagent to each and make up to the 100-ml mark with water. Fill two burettes, C and D, from the flasks C and D, respectively, so that C contains the yellow "phenol blank" solution and D the "phenol standard" solution. The strength of the latter is now such that 1 ml contains 0·00001 g of phenol.

Place 10 ml of the contents of the test tubes A and B (*i.e.*, "sample blank" and "sample") into 50-ml Nessler cylinders, marking these A and B, respectively.

Run, from burette D, a small quantity of the "phenol standard" solution into Nessler cylinder A containing the "sample blank," and run an equal volume from burette C of the "phenol blank" solution into Nessler cylinder B containing the "sample" solution.

Continue adding successive equal volumes of the "phenol standard" and "phenol blank" solutions to the appropriate Nessler cylinders, with intermediate shaking, until the contents of the cylinders are identical in colour. Note the volume in millilitres of "phenol standard" solution required for the colour matching.

NOTE—It is essential that the colour matching operations are performed speedily.

CALCULATION—

Strength of "phenol standard" solution in burette D =

$$5/100 \times 0{\cdot}025 \times 20/25 = 0{\cdot}001 \text{ g per } 100 \text{ ml},$$

or 1 ml of solution ≡ 0·00001 g of phenol.

Volume of sample solution matched in Nessler cylinder =

$$5 \times \frac{10}{25} = 2 \text{ ml}.$$

(Volume of phenol standard solution required to match sample solution) × 0·00001 × 50 = weight in grams of phenol per 100 ml of sample solution = P

Then $P/0{\cdot}00157$ = bromine absorbed by phenol in terms of 0·1 N potassium bromide - potassium bromate = x.

Then total bromine absorption of 100 ml of sample solution in terms of 0·1 N potassium bromide - potassium bromate − x = bromine absorbed by cresol = y.

$y \times 0{\cdot}00236$ = weight in grams of cresol per 100 ml of sample solution = C.

With P and C found, the percentage composition of the free phenols is easily calculated.

EXAMPLE—

Volume of "phenol standard" solution required to match sample = 8·0 ml.

$P = 8{\cdot}0 \times 0{\cdot}00001 \times 50 = 0{\cdot}004$ g of phenol per 100 ml of sample solution.

$$x = \frac{0{\cdot}004}{0{\cdot}00157} = 2{\cdot}55 \text{ ml.}$$

$y = 3{\cdot}00 - 2{\cdot}55 = 0{\cdot}45$ ml.

$C = 0{\cdot}45 \times 0{\cdot}00236 = 0{\cdot}001$ g of cresol per 100 ml of sample solution.

Ratio of free phenol to free cresol = 4 to 1,

or percentage composition of free phenols = 80 per cent. of phenol, 20 per cent. of cresol.

RESINS PREPARED SOLELY FROM *m*- AND *p*-CRESOLS

The special class of resins prepared solely from *m*-cresol and *p*-cresol has been investigated. This requires rather different treatment from the more general class of resins prepared from phenol and cresylic acid.

The problem here is to differentiate between free *m*-cresol and free *p*-cresol, whereas previously the problem was to differentiate between phenol and *p*-cresol.

The initial stages, that is solution of the sample in sodium hydroxide solution, precipitation of the resin by neutralisation to pH 4·5, filtration, and steam distillation of the filtrate, can be carried out as described in the previous method. The steam distillate then contains the free cresols.

A method for determining *m*-cresol and *p*-cresol has been described by Savitt, Goldberg and Othmer.[3] It depends on the formation of the nitrosamine by the action of sulphuric acid and sodium nitrite on a solution of the cresols in acetic acid - potassium acetate buffer, followed by the addition of an excess of alcoholic ammonia to give coloured solutions. In their work known weights of the isolated cresols were dissolved in the buffer solution and aliquots were taken for the colour development. In the problem under consideration, the cresols are in aqueous solution at a relatively low concentration.

However, it has been shown that it is possible to find the concentration of the cresol solution in terms of each isomer by amperometric titration with 0·1 N bromide - bromate solution. By combining this knowledge with a modification of the nitrosamine method, results have been satisfactory.

AMPEROMETRIC TITRATION OF CRESOLS—

Previous experience of the determination of styrene by amperometric titration with bromide - bromate solution by Kolthoff and Bovey's method[5] led us to consider applying a modification of this method to the determination of cresols in aqueous solution. The reason for over-bromination of *o*- and *p*-cresols when determined by Koppeschaar's method is considered to be side-chain substitution. As the reaction rate for nuclear substitution is very much greater than that for the side-chain reaction, it was considered that the small excess of bromine and the short time of standing involved in an amperometric titration should make possible the detection of an end-point at the completion of the nuclear substitution. It was found that amperometric titration of solutions of the *ortho*, *meta* and *para* isomers did in fact give values that agreed well with the theoretical values for the nuclear bromination of the individual isomers. Satisfactory results were also achieved with mixtures of *meta* and *para* isomers and of *meta* and *ortho* isomers.

COMBINATION OF AMPEROMETRIC TITRATION AND NITROSAMINE COLORIMETRIC METHOD FOR THE DETERMINATION OF UNKNOWN MIXTURES OF *m*- AND *p*-CRESOLS IN AQUEOUS SOLUTION—

The concentration of the steam distillate containing the *m*-cresol and *p*-cresol was determined by amperometric titration and the results were calculated in terms of *m*-cresol

and *p*-cresol. This gave the limits between which the concentration of the cresols must lie, even if present as all *m*-cresol or all *p*-cresol.

A suitable aliquot of the steam distillate was then evaporated to dryness with an excess of potassium hydroxide solution, the amount of which was such that on dissolving the residue in acetic acid, the resulting solution had the same proportions of acetic acid, potassium acetate and water as used in the original method. The nitrosamine colour was then developed and the ratio and amount of the isomers determined from a previously prepared calibration chart. The results of a number of determinations are shown in Table I (p. 347).

An attempt to apply the method to mixtures of *o*- and *m*-cresols was unsuccessful, partly owing to difficulty in obtaining reproducible figures for the calibration graphs for the *ortho* isomer and partly because the *o*-cresol and *m*-cresol curves were more closely related and gave less satisfactory differentiation between the isomers.

These conditions would also apply to mixtures of the *ortho* and *para* isomers.

Method for determining total free cresols by amperometric titration

Reagents—

Potassium bromide - potassium bromate, 0·1 N solution—Dissolve 2·780 g of analytical reagent grade potassium bromate and 15·0 g of analytical reagent grade potassium bromide in water and dilute the solution to 1 litre.

Methanol—Add about 10 ml of bromine to 2 litres of methanol and set aside for at least half an hour. Then add zinc dust in small amounts and shake the mixture thoroughly until the excess of bromine has been used up and the methanol is colourless. Filter off the excess of zinc and distil the methanol.

Hydrochloric acid—Analytical reagent grade.

Potassium bromide—Analytical reagent grade.

o-*Cresol*; m-*cresol*; p-*cresol*—B.D.H. Laboratory Reagent grade, redistilled before use.

Procedure—

Transfer an aliquot of the steam distillate containing the cresols and prepared as described on p. 342 to a 400-ml tall beaker containing 100 ml of methanol, 10 ml of concentrated hydrochloric acid and about 2 g of potassium bromide. Add sufficient water to make a total of 100 ml with the aliquot of cresol solution used. Then raise the beaker to immerse the platinum electrode and the salt bridge from the calomel cell and start the rotating platinum electrode. Note the ammeter reading and add 0·1 *N* potassium bromide - potassium bromate solution from a burette. Take ammeter readings at intervals during the titration and, when the end-point is approached, as shown by the slower rate of decrease of current after additions of titrant, make the additions in increments of 0·5 ml and take the ammeter readings 1 minute after each addition. When a number of additions have been made with increasing ammeter readings, plot the readings against volume of titrant added; the end-point is at the intersection of the straight lines through points before and after the end-point.

If the volume of 0·1 *N* potassium bromide - potassium bromate required = V ml and the volume of steam distillate = v ml,

then, total cresols calculated to *p*-cresol = $\frac{2{\cdot}7V}{v}$ mg per ml

and total cresols calculated to *m*-cresol = $\frac{1{\cdot}8V}{v}$ mg per ml.

Results—

The results for a number of titrations of the individual isomers and for mixtures of isomers are shown in Table I.

Method for determining the ratio of free *p*-cresol to free *m*-cresol

Reagents—

Potassium hydroxide, N.

Acetic acid, 80 per cent. v/v—Dilute 800 ml of glacial acetic acid to 1 litre with water.

Sulphuric acid, concentrated—Analytical reagent grade.

Sodium nitrate solution—A saturated aqueous solution.

Alcoholic ammonium hydroxide—Mix 300 ml of ammonium hydroxide, sp.gr. 0·880, 250 ml of water and 450 ml of ethyl alcohol.

o-*Cresol*; m-*cresol*; p-*cresol*—B.D.H. Laboratory Reagent grade, distilled before use.

Cresol stock solutions, 1 per cent.—Weigh accurately about 2·5 g of each cresol isomer into a 250-ml calibrated flask, dissolve each in water and dilute to the mark.

Cresol standard solutions—Dilute an aliquot of the stock solution to 100 ml in a graduated flask to give a solution of which 1 ml contains 1 mg of cresol.

PREPARATION OF CALIBRATION GRAPHS—

From a micro-burette put volumes of 0·6, 0·8, 1·0, 1·2 and 1·4 ml of the standard cresol solution into 50-ml calibrated flasks. Add 1·4 ml of *N* potassium hydroxide and evaporate the solution to dryness by heating it on a water-bath and drawing a current of air through the flask by means of a glass tube inserted in the flask and connected to a water pump. Dissolve the residue in 5 ml of 80 per cent. acetic acid solution. To this solution add 5 drops of concentrated sulphuric acid and then 2 drops of saturated sodium nitrite solution and mix by swirling. Set the mixture aside for 20 minutes. Then cool the flask in an ice-water mixture and slowly add alcoholic ammonium hydroxide from a burette until the volume is slightly less than 50 ml. Set the solution aside overnight, then dilute it to the 50-ml mark with alcoholic ammonium hydroxide solution and measure the optical density on a Spekker absorptiometer with Ilford No. 602 spectrum blue filters and 1-cm cells and with water as the reference liquid.

In our work the following Spekker absorptiometer readings were recorded—

	Indicator drum reading for				
	0·6 mg	0·8 mg	1·0 mg	1·2 mg	1·4 mg
p-Cresol	0·206	0·279	0·336	0·396	0·478
m-Cresol	0·022	0·039	0·051	0·057	0·065
o-Cresol	0·168	0·209	0·267	0·315	0·356

The straight line graphs for the *para* and *meta* isomers relating indicator drum readings to milligrams of cresol per 50 ml of solution were drawn. Intermediate straight lines were drawn between the two graphs to give 10 equal intercepts; these graphs represent mixtures of the isomers containing 10 per cent., 20 per cent. . . . 80 per cent. and 90 per cent. of *p*-cresol.

PROCEDURE—

Having found the volume of 0·1 *N* potassium bromide - potassium bromate, *V*, required to brominate a volume *v* of the steam distillate by amperometric titration, measure an aliquot of the steam distillate equal to about $v/2{\cdot}25\ V$ ml (see Note below) into a 50-ml calibrated flask. Add 1·4 ml of *N* potassium hydroxide solution and evaporate the solution to dryness on a water-bath, assisting the evaporation by drawing a current of air through the flask. Develop the nitrosamine colour and measure the optical density in terms of Spekker absorptiometer readings as described in the preparation of the calibration graphs.

From the concentration of the solution in terms of *m*- and *p*-cresols as calculated from the 0·1 *N* bromide - bromate titration and the volume of solution taken, calculate the weight of cresol in terms of the *meta* and *para* isomers in the aliquot of the steam distillate taken. Draw a straight line joining the points on the *m*-cresol and *p*-cresol graphs corresponding to these weights of *m*- and *p*-cresol, respectively. Mark on this line the point corresponding to the indicator drum reading. Calculate the percentage of *p*-cresol from the position of the point in relation to the intermediate graphs. Also read from the graph the total cresols present and calculate the concentrations of *m*-cresol and *p*-cresol in the steam distillate. From the weight of sample taken, calculate the percentage of free *m*- and *p*-cresol present in the sample and the ratio of free *m*-cresol to free *p*-cresol.

NOTE—As the concentration of cresols calculated to *p*-cresol = $2{\cdot}7\ V/v$ mg per ml
and the concentration of cresols calculated to *m*-cresol = $1{\cdot}8\ V/v$ mg per ml,
the mean value for this expression becomes $2{\cdot}25\ V/v$ and therefore
1 mg of a 1 + 1 mixture of *m*-cresol and *p*-cresol would be present in a volume of $v/2{\cdot}25\ V$ ml.

RESULTS—

Some results of amperometric titrations of aqueous solutions of *o*-, *m*- and *p*-cresols are shown in Table I.

TABLE I

AMPEROMETRIC TITRATION OF AQUEOUS SOLUTIONS OF *o*-, *m*- AND *p*-CRESOLS

Isomer	Weight of cresol g	0·1 *N* potassium bromide - bromate required: found, ml	0·1 *N* potassium bromide - bromate required: calculated, ml	Bromine atoms combining with 1 molecule of cresol: found	Bromine atoms combining with 1 molecule of cresol: calculated
ortho ..	0·0300	10·98 11·00	11·11	1·98 1·98	2·00
meta ..	0·0404	22·22 22·30 22·34	22·33	2·97 2·98 2·98	3·00
para ..	0·0400	14·78 14·70 14·68	14·82	1·99 1·98 1·98	2·00
para ..	0·0605	22·37	22·41	2·00	
Mixture *ortho* ..	0·0200	11·11	11·34	2·21	2·26
Mixture *meta* ..	0·0071	11·03		2·20	
Mixture *ortho* ..	0·0150	13·61	14·02	2·43	2·50
Mixture *meta* ..	0·0152	13·58		2·43	
Mixture *para* ..	0·0226	19·20	19·60	2·42	2·47
Mixture *meta* ..	0·0202	19·30		2·44	
Mixture *para* ..	0·0265	20·04	20·14	2·40	2·41
Mixture *meta* ..	0·0186	20·06		2·40	
Mixture *para* ..	0·0545	23·12	23·59	2·06	2·08
Mixture *meta* ..	0·0061	23·16		2·07	

TOTAL CRESOLS AND PERCENTAGE OF *p*-CRESOL FOUND IN AQUEOUS SOLUTION CONTAINING KNOWN AMOUNTS OF *m*- AND *p*-CRESOLS—

A series of solutions containing *p*-cresol and *m*-cresol were prepared by diluting known volumes of stock solutions of individual cresols to 500 ml, and the ratio of the isomers and the total concentration were determined in each solution. The results are shown in Table II.

TABLE II

DETERMINATION OF RATIO OF THE ISOMERS AND TOTAL CONCENTRATION IN AQUEOUS SOLUTIONS OF MIXED *p*- AND *m*-CRESOLS

Amount of cresol taken in 500 ml of solution: *p*-cresol, g	*m*-cresol, g	total, g	Calculated proportion of *p*-cresol, %	Total cresols found, per 500 ml of solution, g	Proportion of *p*-cresol found in mixture, %
0·3025	nil	0·3025	100	0·3042	102
				0·3040	101
0·2950	0·1083	0·4033	73	0·3960	73
				0·4020	76
0·1514	0·1532	0·3046	50	0·2964	49
				0·3029	45
0·0757	0·2298	0·3055	25	0·3167	22
				0·3207	27

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September 23rd, 1952

The Determination of Iodine in Blood Serum

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The practical aspects of the micro-determination of iodine in serum by the method originally proposed by Chaney in 1940 are discussed, and certain modifications are suggested to ensure smooth working and good recovery of iodine. The complete procedure is described and experimental results bearing on reproducibility and accuracy, together with the iodine levels in the sera of normal individuals, are recorded.

It is now generally accepted that thyroid activity is directly related to the iodine level in the blood serum and that the relationship is more specific for the protein-bound organic fraction than for the total iodine. Consequently a reliable method ought to be available for the determination of iodine.

Among the methods proposed for this purpose that of Chaney[1] has attracted most attention, by reason of the introduction of a still designed for isolating the iodine by volatilisation in a minimum volume of distillate and the use of the catalytic action of iodide on the reduction of ceric sulphate by arsenious acid for the final colorimetric step. The latter is a sensitive means of determining iodide, especially suited to the micro-amounts met with in serum, whilst the Chaney Still greatly enhanced the practicability of the comparatively rapid wet digestion method. In Chaney's procedure organic matter is destroyed and iodine, in all forms, is oxidised to iodate by digestion with a mixture of chromic and sulphuric acids. The iodine is volatilised by reducing the digest at boiling point with phosphorous acid, is trapped in an absorbing solution and is finally determined colorimetrically by the reaction mentioned above.

It has become obvious that, in practice, even a relatively simple procedure must be rigidly standardised in order to obtain reliable results; the best technique is still a matter of conflicting opinion. It seems relevant, therefore, to make some contribution to the practical aspects of the determination from observations made in the course of four years' experience of its application in clinical work. The method discussed and described here is similar to that of Barker,[2] but has some additions and modifications, that, it is believed, remove most of the causes of erratic results and tend to make its routine use practicable.

Practical considerations

Digestion and absorption—

Chaney's method was elaborated in detail by Taurog and Chaikoff,[3] but their procedure was criticised by Barker,[2] especially for its use of sodium hydroxide solution to absorb the volatilised iodine. Barker stated that absorption in a reducing medium is essential for ensuring good recovery of iodine; he used a solution of sodium sulphite, subsequently removing sulphur dioxide by acidifying and aerating the distillate. He later eliminated the aeration step by using a sodium hydroxide solution containing added arsenious oxide.[4] The addition of arsenious oxide has been approved by Thomas, Shinn, Wiseman and Moore,[5] but Moran[6] has rejected it upon the ground that it causes a non-specific reduction of ceric sulphate. Moran reverted to sodium hydroxide by itself; he obtained a good recovery of iodine by carefully controlled heating during digestion and by adding hydrogen peroxide to the phosphorous acid used for reduction.

We have found sodium hydroxide to be a generally unsatisfactory absorbent, but potassium hydroxide has given distinctly better results. It is interesting to note that Connor, Curtis and Swenson[7] have apparently obtained satisfactory results with potassium hydroxide. Sodium sulphite alone and potassium hydroxide solution containing added arsenious oxide have also given uniformly good recoveries; the latter has been used exclusively for a considerable time. Although a small non-specific reduction of the ceric sulphate occurs, it is never serious enough to jeopardise accuracy, and any slight disadvantage from this effect is considerably outweighed by its beneficial influence upon recovery of iodine. Moran's finding that the manner and degree of heating are of paramount importance to the successful use of sodium hydroxide suggests that the addition of the reducing agent also introduces a certain degree of much-needed flexibility in technique, for it is then only necessary to avoid

excessive heating, as denoted by the appearance of dense white fumes, which, as pointed out by Barker, are especially disastrous during the second heating. It is difficult to standardise heating, but it has been found sufficient, both for adequacy of heating and for provision of a safety factor against loss, to discontinue heating when the flask is distinctly, but not densely, filled with fumes. Besides this moderation in heating, it is important to provide an adequate excess of chromic acid for digestion, as complete reduction of the chromic acid leads inevitably to loss of iodine.

REAGENTS—

The main difficulty likely to be encountered in setting up and in long term use of the method is that of obtaining reagents of sufficient purity. The sensitivity to iodide of the rate of the ceric sulphate - arsenious acid reaction decreases rapidly under the test conditions when amounts of iodide in excess of 0·15 μg are used, so that accuracy and working range are dependent upon a low initial blank value. Little progress appears to have been made in overcoming this difficulty, the general procedure being to test specimens of chemicals from various manufacturers until a satisfactory combination is found, without any regard to the suitability of subsequent deliveries from the same sources.

It is generally agreed that ordinary distilled water can be freed from iodine by re-distillation from alkali in an all-glass still; the water used in the determination and in the preparation of the reagents should be purified in this manner, although the apparatus may be rinsed with distilled water as ordinarily prepared. Concentrated sulphuric acid can be purified if necessary by boiling it with a little hydrochloric acid for one to two hours in a fume chamber,[3] but this procedure has fortunately so far proved unnecessary. Most trouble has been experienced with chromic acid, phosphorous acid and arsenious oxide; chromic acid is always contaminated, usually to the extent of being unusable, whilst the quality of the other two reagents varies according to source and even to batch. Boiling the solution of phosphorous acid for a period of a half to one hour is usually recommended for removing contamination, but we have found this to be of no value, unusable specimens of phosphorous acid showing no improvement after boiling for several hours.

Experimental work has shown that it is possible by simple purification procedures to eliminate uncertainty in the use of phosphorous acid and arsenious oxide, but the only satisfactory solution of the problem created by the general impurity of chromium trioxide has been to replace it with sodium dichromate. The technical grade of sodium dichromate is usually sufficiently free from contaminants to be used directly, but a poor specimen can be improved by washing the powdered solid with absolute industrial alcohol, drying at 120° C and using 87·5 instead of 100 g as described for the preparation of the reagent (p. 351). Phosphorous acid is purified by treatment with activated charcoal under specified conditions, and arsenious oxide is re-sublimed before use. Details of the methods are included in the reagent section of the procedure (p. 350). The use of these methods has contributed largely to the uniformly low blank value obtained during the past two years with various batches of materials.

STILL—

The use of a special form of still is essential to success. The alternative of prolonged distillation followed by evaporation, besides being tedious, may also cause chromium compounds in the distillate to be present to such an extent that it is difficult to prevent interference with the colorimetric reaction. The design of the still has inevitably provoked some rather specialist apparatus, but there is no evidence that efficiency must be divorced from simplicity.

The original Chaney still was awkward to manipulate, but was improved by Talbot, Butler, Saltzman and Rodrignez[8], who provided a tap for removing the absorption liquid. A further modified form of still* has been used in this laboratory (Fig. 1), the modification including the addition of a stoppered inlet to the trap to permit introduction of the absorption solution with the apparatus completely assembled and replacement of the splash baffle-plate and return tube of the original still by a closely fitting internal funnel that performs both functions.

In this form the still is simpler to construct and manipulate and is no more trouble to set up and dismantle than a small Soxhlet apparatus. It is important to note with regard to the construction that the glass stopper and stopcock must be made of the same type of glass

* The still is supplied by Messrs. Baird and Tatlock (London) Ltd., and was designed in collaboration with their technical staff.

as the rest of the still if sticking is to be avoided. When completely assembled the top socket of the still carries a reflux condenser and the bottom joint is plugged into the socket of a two or three-necked 500-ml round-bottomed flask, which also carries a dropping funnel. The three-necked flask is suggested because it is a standard product and consequently more easily obtainable; the third neck is closed with a glass stopper. This flask also serves as the digestion flask.

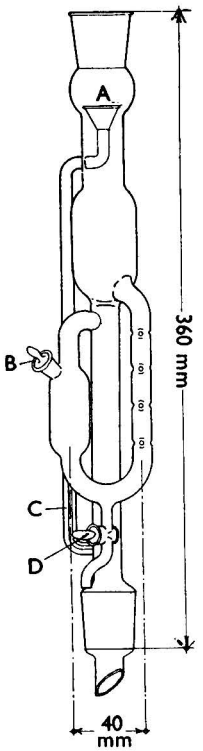

Fig. 1. Modified Chaney still. A, combined splash baffle and return tube; B, stoppered inlet to trap; C, capillary for regulating reflux action; D, outlet tap from trap

COLORIMETRIC DETERMINATION—

The precise practical details for carrying out this final step in the determination apparently vary from one laboratory to another, the essential factors being accurate measurement of volumes and strict control of temperature and time of reaction. Volumes of distillate and reagents and the time of reaction have been chosen in this laboratory to enable absorption measurements to be made in a standard 1-cm glass cell over a useful working range at a temperature of 37° C by means of either a Spekker or a Biochem absorptiometer. Provision has also been made for the following considerations—

1. Addition of sodium chloride to the reaction mixture, for enhancing the catalytic activity of the iodide and eliminating the random effect of traces of chlorides that may appear in the distillate, can be made with advantage, as recommended by Barker.[2]
2. The modification suggested by Carr, Graham, Ober and Riggs[9] has a marked beneficial effect upon the stability of the blank reading and merits more general attention. This consists in adding sulphuric acid up to a concentration of approximately 2·3 *N* in the final reaction mixture in order to inhibit the catalytic effect of traces of chromium compounds that may have collected in the distillate. The necessary acid is incorporated in the arsenious acid reagent.
3. A standard graph is prepared from the readings given by addition of standard iodide solution to blank distillates. This procedure was used by Taurog and Chaikoff[3] and is preferable to the addition of iodide to water, used by Barker,[2] as deviations of up to 10 per cent. may occur, notably with the larger amounts of iodide, when the readings given by similar amounts of iodide by the two methods are compared.

METHOD

COLLECTION OF BLOOD—

Venous blood is allowed to clot and the serum separated by centrifugation in the usual manner, but it is advantageous to maintain aseptic conditions throughout, as the serum will then keep unchanged for at least a fortnight if stored at 4° to 6° C.

REAGENTS—

Water—Make ordinary distilled water alkaline with potassium hydroxide, add some marble chips to prevent bumping, and distil from an all-glass apparatus. Use the distillate for all reagents and in the procedure.

Sulphuric acid, 70 per cent.—Add 600 ml of concentrated sulphuric acid (Hopkin and Williams Ltd. AnalaR) cautiously, with cooling, to 450 ml water.

Phosphorous acid, 50 per cent. w/v—Melt together 500 g of crystalline phosphorous acid and 100 ml water by warming in a beaker on a water-bath. Add 5 g of "Norit" charcoal with stirring, and set aside with frequent stirring for about 10 minutes. Filter through a Whatman No. 54 filter-paper, returning the first portions of filtrate until clear and colourless. Allow

the filter to drain at the end of filtration; do not wash it. Dilute the filtrate to 1 litre with water.

Sodium dichromate solution—Dissolve 100 g of commercial sodium dichromate (Hopkin and Williams Ltd. AnalaR) in a mixture of 200 ml of water and 5 ml of 70 per cent. sulphuric acid.

Arsenious acid reagent—Heat about 10 g of arsenious oxide in a porcelain dish, covered with a clock glass, over the free flame of a micro-burner in the fume chamber, until the major part has sublimed and condensed on the sides of the dish, remove and store in a clean bottle. Dissolve 3·71 g of the re-sublimed arsenious oxide in 50 ml of *N* sodium hydroxide solution in a 1-litre calibrated flask and dilute with about 400 ml of water. Add slowly with shaking and cooling 425 ml of 70 per cent. sulphuric acid, make up to the mark with water and mix. Dissolve 3·125 g of pure sodium chloride in this solution.

Absorption solution—Dissolve 0·75 g of the re-sublimed arsenious oxide in 100 ml of water containing 2·5 g of potassium hydroxide.

Ceric ammonium sulphate reagent—Mix 17 g of ceric ammonium sulphate with about 300 ml of water in a 500-ml calibrated flask and add, slowly, with mixing, 80 ml of 70 per cent. sulphuric acid. Set aside with occasional mixing until solution is complete, make up to the mark with water and mix.

Sodium hydroxide solution, 0·5 N.

Zinc sulphate solution[10]—Prepare a 10 per cent. w/v solution of crystalline zinc sulphate and titrate 10 ml of it with the 0·5 *N* sodium hydroxide solution. From 10·8 to 11·2 ml of the latter should be required to produce a pink colour with phenolphthalein.

Standard solutions—Dissolve 0·131 g of pure potassium iodide in water and make up to 100 ml. Dilute 5 ml of this solution to 500 ml to provide a stock solution containing 10 μg of iodine per ml. Dilute 5 ml of stock solution to 500 ml to obtain a convenient working solution containing 0·1 μg of iodine per ml. These solutions are reasonably stable if kept away from light in closely stoppered bottles.

PROCEDURE—

Precipitation of protein-bound iodine—To 2 ml of serum in a 50-ml centrifuge tube add 20 to 30 ml of water, 2 ml of zinc sulphate solution and 2 ml of 0·5 *N* sodium hydroxide; mix after each addition. Centrifuge, discard the supernatant liquid, stir the precipitate thoroughly with about 30 ml of water, centrifuge again and discard the water. Make two further washings with water. Dissolve the precipitate in about 5 ml of 70 per cent. sulphuric acid and transfer the solution to the digestion flask. Wash the centrifuge tube with several further portions of acid until a total volume of 25 ml has been used.

Total iodine—If it is required to determine the total iodine, transfer 2 ml of serum directly into the digestion flask by means of a pipette and add 25 ml of 70 per cent. sulphuric acid.

Digestion—To the acid contents of the flask add 5 ml of sodium dichromate solution and some glass beads, and heat over a moderately hot bunsen burner on an asbestos-centred gauze in the fume chamber until fumes (not dense, see p. 349) of sulphuric acid fill the flask. Allow to cool for a short period, then add 15 ml of water and repeat the heating. Allow to cool.

Distillation—To the digest add 30 ml of water and assemble the still completely, placing 6 ml of phosphorous acid in the dropping funnel. Heat to brisk boiling and, when the whole of the still is heated by steam (this condenses freely from the reflux condenser), run out the condensate from the trap and discard it. Unstopper the trap inlet and introduce 1·0 ml of absorption solution, replace the stopper and immediately run the phosphorous acid rapidly dropwise into the boiling digest. Allow the distillation to continue for 10 minutes, remove the burner and run off the distillate into a glass-stoppered tube calibrated at 20 ml. Remove the reflux condenser and wash the sides of the still with three successive portions of about 2 to 3 ml of water delivered conveniently from a pipette, adding the washings to the distillate. Cool, adjust the volume of distillate to 20 ml with water and mix.

Colorimetry—Transfer 5-ml aliquots of distillate into test tubes approximately 1·5 cm in diameter by means of a pipette, add 2 ml of water and 2 ml of arsenious acid reagent, mix and place in a water-bath at 37° $\pm$ 0·1° C. Allow about 10 minutes for the temperature of the test solutions to reach that of the bath and then add 1·0 ml of ceric ammonium sulphate solution to each tube, allowing an interval of 45 to 60 seconds after each addition. After exactly 15 minutes from the first addition measure the optical density of the first tube and then the others, at the appropriate intervals, in a 1-cm glass cell and with a violet filter. From

the readings, calculate the amount of iodine present in the test solution by means of a standard graph. Prepare a standard graph as follows: pool the distillates of two blank determinations, made by omitting the serum, and to six 5-ml aliquots add 0, 0·2, 0·4, 0·6, 0·8 or 1·0 ml of standard iodide solution containing 0·1 μg iodine per ml. To each tube add sufficient water to bring the volume to exactly 7 ml. Add 2 ml of arsenious acid reagent to each tube and proceed as above with additions of ceric ammonium sulphate. Plot the readings against micrograms of added iodine.

Note—With a Spekker absorptiometer, Ilford 601 filters are used, but as this filter cannot be used with a Biochem absorptiometer, a similar working range with a Chance OB 1 filter can only be obtained by increasing the concentration of ceric ammonium sulphate. This concentration may be increased up to double the original strength, without seriously affecting accuracy, by using 34 g instead of 17 g in the preparation of the reagent described above.

Results

Reproducibility and recovery—

The few available reports from other laboratories have dealt in somewhat vague terms with the order of accuracy to be expected from this type of method. Barker[2] gives experimental means showing a recovery averaging 90 per cent. with a range of 87 to 95 per cent. Thomas *et al.*[5] recover 94 to 100 per cent. of added iodide, but give no details. Moran[6] reports 88 to 94 per cent. recoveries of iodide added to serum and concludes that 100 per cent. recovery is unattainable.

Evaluation of the method proposed has been made by adding iodine to serum in the form of iodide and pure sodium L-thyroxine pentahydrate. The pooled serum had an iodine content just below the normal range, by reason of inclusion of some serum from hypothyroid patients. As it is our practice to carry out duplicate determinations on each specimen, the variation in the means of duplicates has been recorded here, ten duplicate determinations being made on different occasions at each of three iodine levels giving a range embracing those values found in practice except in severe hypothyroidism and thyrotoxicosis.

The amounts of iodine found in 5-ml aliquots of distillate before and after additions to the serum are shown in Table I; the highest, lowest and mean values are the means of simultaneous duplicate determinations, and the standard deviations are for the means of the ten replicates.

Table I

Addition of iodine to serum

Substance added	Iodine added, μg	Iodine found			Standard deviation, μg	Mean recovery, %
		Highest, μg	Lowest, μg	Mean, μg		
Nil	Nil	0·017	0·013	0·0155	± 0·0012	—
Potassium iodide ..	0·025	0·043	0·039	0·0415	± 0·0011	104
	0·050	0·068	0·062	0·0650	± 0·0016	98
Sodium L-thyroxine	0·025	0·042	0·037	0·0395	± 0·0014	96
	0·050	0·070	0·062	0·0665	± 0·0018	102

The over-all mean recovery of iodine in 40 duplicate determinations is thus 100 per cent.; the comparatively small rise in the standard deviation with increase in the iodine level suggests that variations are due to a constant experimental error rather than to fluctuations in recovery. On expressing the results as micrograms of iodine per 100 ml of serum, the means of duplicate determinations show a standard deviation of ±0·25 over the range 3 to 8, increasing to ±0·35 at 13. Increased accuracy in determining the lower levels of iodine, such as occur in hypothyroidism, can be attained by using 3-ml instead of 2-ml quantities of serum and precipitating the proteins with 3 ml each of the zinc sulphate and 0·5 *N* sodium hydroxide solutions. At the higher levels any advantage gained by working with greater amounts of iodine is largely offset by the decrease in sensitivity of the colorimetric reaction.

Normal values—Determination of the protein-bound iodine has been made upon the sera of 40 normal healthy individuals. The values obtained ranged from 3·9 to 7·8 μg per 100 ml with a mean value of 5·9 and a standard deviation of ±0·85. The suggested normal range is 3·5 to 8·5 μg per 100 ml.

The author expresses his thanks to the Trustees of the London Clinic for providing facilities for this work, and to Glaxo Laboratories Ltd. for a gift of pure sodium L-thyroxine pentahydrate.

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November 14th, 1952

A Colorimetric Method for the Micro-determination of Potassium in Serum

By S. BAAR

Potassium in serum is precipitated with sodium cobaltinitrite without prior de-proteinisation. The precipitated complex salt is dissolved in sulphamic acid, which destroys the excess of nitrous acid. The 8-hydroxyquinoline complex of cobalt is formed and extracted into chloroform, the absorption maximum at 403 mμ being used for the colorimetric determination.

The coloured complex is stable, and its absorption obeys Beer - Lambert's law over a fairly wide range. Recovery experiments and comparison of a series of replicate determinations with a widely used colorimetric method show a maximum deviation of 1 per cent. from expected values.

The potassium of biological fluids is most commonly precipitated as potassium sodium cobaltinitrite, as suggested by Kramer and Tisdall,[1] or as potassium silver cobaltinitrite as suggested by Breh and Gaebler.[2] The composition of the silver complex is affected by the sodium chloride content of the medium, so that it seemed preferable to precipitate the potassium by the method described by Kramer and Tisdall[1] and Abul-Fadl.[3] The composition of the complex, which should be $K_2NaCo(NO_2)_6.H_2O$, is affected by the potassium concentration,[4] which is consequently kept within a narrow range.

The potassium in the precipitate is determined indirectly. Methods have been described in which nitrous acid is liberated and estimated, but these are unsatisfactory owing to the volatility of the nitrous acid. In the most reliable methods, the cobalt in the precipitate is determined colorimetrically, as, for example, by its reaction with nitroso-R-salt in hot acetic acid solution,[5,6] but the red colour so formed fades with time. Another method has been described by Abul-Fadl,[3] but the maximal intensity of the reaction product is only attained after 10 to 15 minutes at 37° C.

In this paper is described a sensitive colorimetric method that overcomes some of the difficulties mentioned above. The cobalt content of the precipitated potassium sodium cobaltinitrite is determined by its reaction with 8-hydroxyquinoline. With cobalt a stable chelate compound is formed, which is readily soluble in polar solvents but almost insoluble in water. The complex is formed at pH values between 4·3 and 11·6, and the reagent is sensitive to 1 part in 100,000, according to Welcher.[7]

Method

Reagents—

Cobaltinitrite reagent—Dissolve 120 g of analytical reagent grade sodium nitrite in 180 ml of distilled water. Add 210 ml of this solution to 50 ml of distilled water containing 25 g

of hydrated cobalt nitrate and 12·5 ml of glacial acetic acid. Aspirate air through the reagent until it is free from nitrous oxide fumes. Centrifuge the reagent before use and keep it in a refrigerator. It can be used for 2 months.

Ethyl alcohol—Add 30 ml of distilled water to 70 ml of absolute ethyl alcohol.

Ammonium hydroxide, 2·2 N—Make an approximately 13 per cent. aqueous dilution of ammonium hydroxide, sp.gr. 0·880.

Sulphamic acid—Dissolve 5 g of sulphamic acid (amino-sulphuric acid) in 100 ml of distilled water.

8-*Hydroxyquinoline*—Dissolve 2 g of analytical reagent grade 8-hydroxyquinoline in 100 ml of absolute ethyl alcohol.

Chloroform—C.P.

PROCEDURE—

Wash 0·1 ml of serum into 0·5 ml of distilled water in a wide centrifuge tube. Add 1·0 ml of the cobaltinitrite reagent and set the mixture aside at room temperature for 1 hour. Then add 1·0 ml of distilled water and centrifuge the tube and contents at 1800 r.p.m. at a radius of 15 cm for 5 minutes. Carefully decant the supernatant fluid and wash the precipitate thrice with 1-ml portions of 70 per cent. ethyl alcohol, the final centrifugation being at 3000 r.p.m. for 10 minutes. Then remove the supernatant fluid as completely as possible by draining the tube mouth-downwards on filter-paper. Finally dry the walls of the tube with filter-paper. Dissolve the precipitate in 2 ml of the sulphamic acid solution, which destroys the excess of nitrous acid. Warm the tube for 30 seconds on a bath of boiling water, and then add 4 ml of distilled water, thoroughly mix the contents of the tube and transfer 5 ml to another centrifuge tube. Add 1 ml of 2·2 *N* ammonium hydroxide, swirl the solution, and then add 0·5 ml of 8-hydroxyquinoline reagent. The final pH value is 9·5. Extract the complex by shaking this solution with 4 ml of pure chloroform. Siphon off the aqueous layer and filter the turbid chloroform layer through a 4·25-cm Whatman No. 1 filter-paper folded and placed over the mouth of a tube without insertion into a funnel. The solution

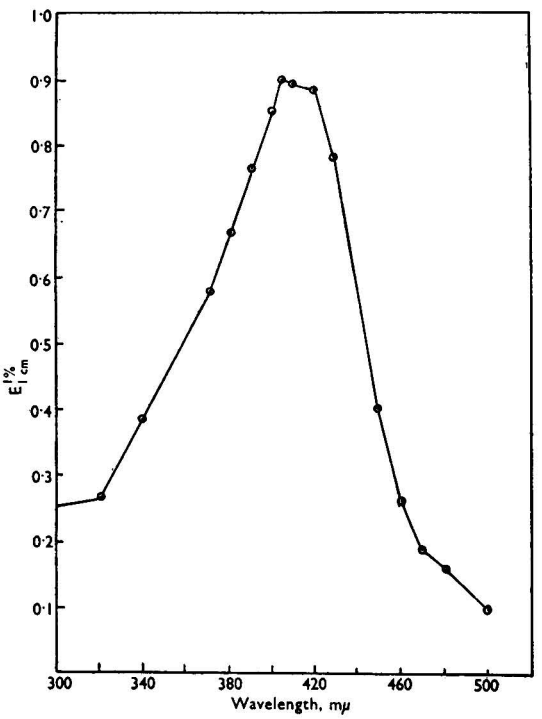

Fig. 1. Absorption graph of cobalt hydroxyquinolate

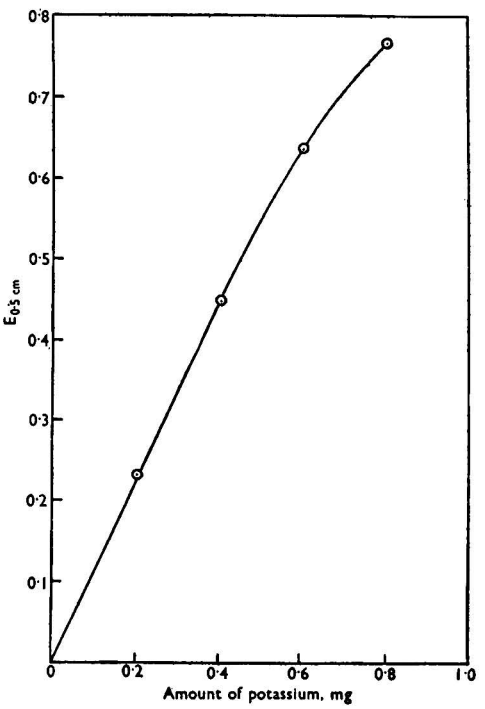

Fig. 2. Typical calibration graph for serum potassium

is then ready for colorimetric examination. The absorption maximum of the cobalt hydroxyquinolate lies at 403 mμ, as determined with a Unicam quartz spectrophotometer (Fig. 1).

Throughout this study a Spekker photo-electric absorptiometer was used with the standard projector-type lamp and a combination of Ilford 601 and Kodak Wratten 35 filters. The Kodak filter was used in place of the usual Chance ON 20 heat-absorption filter.

Calibration graph—

Analytical reagent grade potassium sulphate was dried to constant weight and its purity was found to be 99·35 per cent. by gravimetric determination as potassium platinichloride. From this material a standard solution containing 0·2 mg of potassium per millilitre was made and used in the preparation of the typical calibration graph shown in Fig. 2.

Experimental

Effect of dilution—The effect of dilution on precipitation was investigated by adding to a constant amount of standard potassium solution various amounts of distilled water. The final concentration of the cobaltinitrite reagent was kept in the range of 50 to 77 per cent. The colorimeter readings over this range were within the experimental error. The mean concentration, 67 per cent., was chosen for the working conditions.

Stability—The stability of the coloured complex was investigated by recording the colorimeter readings at intervals of 15 minutes. After 2 hours, the readings deviated by not more than 1 per cent. from those recorded initially.

Reproducibility—The reproducibility of the values recorded and their agreement with the results by an accepted colorimetric method were investigated. A specimen of venous whole blood was taken and the serum was separated in the usual way. Twelve replicate determinations were made by the method described and the results were compared with those of twelve replicate determinations made by the method described by King.[8] The proposed method showed a range of 17·50 to 17·85 mg per 100 ml, with a mean of 17·70 mg, compared with a range of 17·50 to 18·00 mg per 100 ml and a mean of 17·82 mg found by King's method. The standard deviation of the author's method was found to be 0·154 mg per 100 ml, compared with 0·104 mg for King's method. The standard error of the difference was 0·185 mg per 100 ml (P = 0·5), which showed no significant difference.

Recovery of added potassium—

The initial potassium content of a 10-ml sample of serum was established by triplicate estimations; 4·45 mg of dried potassium sulphate were then dissolved completely in 5 ml of the serum. The results of the recovery experiment are shown in Table I.

Table I

Recovery of potassium added to serum as potassium sulphate

Potassium in original serum, mg per 100 ml: 15·0, 15·2, 15·0 (average, 15·07)

Potassium in serum to which 20 mg per 100 ml had been added		
Found, mg per 100 ml	Expected, mg per 100 ml	Deviation from expected, %
35·02	35·07	−0·14
35·08	35·07	+0·03
35·10	35·07	+0·08

Comparison with King's method—

Twelve samples of venous blood were taken from twelve patients chosen at random. Determinations in duplicate were made on each sample both by the proposed method and by King's method. The results were the same in four out of twelve samples, whilst the percentage deviation of the remainder ranged from −0·905 to +0·620.

The percentage recovery of added potassium sulphate, as indicated by Table I, was within 0·2 per cent. of the expected figure. Comparison of a series of determinations showed a maximum deviation of 1·0 per cent. from the expected value. The proposed method can

therefore be recommended for the determination of potassium in serum. It has the advantage over existing chemical methods of being more economical of serum, and the stability of the colour is high without undue complication of the working procedure.

I should like to thank the Unit Director, Dr. J. P. Bull, for permission to carry out this work and for his help in the statistical treatment of the data. Thanks are also tendered to Mr. D. M. Jackson for permission to take samples of venous blood from patients in his care.

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October 15th, 1952

A Scheme of Semi-micro Qualitative Analysis for Thirty-nine Elements

By H. Holness and K. R. Lawrence

The classical hydrogen sulphide scheme of qualitative analysis is modified to include all the elements likely to be encountered in modern analytical practice.

The behaviour of tungsten in forming complex acids is recognised and allowed for.

An existing method of phosphate removal is modified and expedited to deal both with phosphates and complex tungstates.

The details given apply only to the semi-micro technique for 2 to 5 mg of material in about 3 ml of solution.

In the past two decades the greatly increased use of the less familiar elements has brought about a gradual change in our conception of a "rare" element. Titanium, zirconium, molybdenum and tungsten are examples of elements still rare by textbook standards but in common use. The usual systematic scheme of qualitative analysis, as taught in schools and universities, has a background of tradition that ensures its continuance. Nevertheless, with modifications, it can be made to include most of the recently developed elements.

The classical scheme of Noyes and Bray,[1] although comprehensive as regards the number of elements, departs entirely from the traditional elementary system. The same criticism can be levelled at other, less comprehensive, schemes that have appeared since[2]; no scheme appears to take into consideration, and allow for, the behaviour of tungsten in forming heteropoly acids.

The modifications described in detail below are those necessary to convert a simple classical scheme, such as one recently published,[3] into a scheme embracing all the elements likely to be encountered in modern analytical practice. It makes provision for the complex poly-acids of tungsten and requires only those reagents that are normally found in an analytical laboratory. For 2 to 3 ml of solution containing from 2 to 5 mg of solid, the scheme, in the hands of senior students, has given good results with mixtures containing as many as ten

elements. There is reason to believe that the scheme will be equally applicable to work carried out on the macro scale, but so far only the semi-micro technique has been used.

Except for the silver group of metals—the traditional group 1—the groups remain as in the elementary scheme; they are merely extended to accommodate the additional elements. This means that the group separations have been modified to allow for the extra elements. The silver group has been distributed between the hydrogen sulphide group (group 2) and the "insolubles"; its place is taken by a new group 1, which includes metals easily reduced to their elemental form by hydrazine in hydrochloric acid solution.

Method

A. Preparation of solution and treatment of insolubles—

Boil 2 to 5 mg of the substance with 1 ml of a mixture of equal volumes of concentrated hydrochloric acid and bromine water until the excess of bromine is removed. Add an equal volume of water, boil and remove any insoluble material. Reserve the hot solution for the group separations (see B below). Wash the insoluble portion with water, dry it and transfer it to a piece of nickel foil, add half a pellet of sodium hydroxide and fuse.

Cool the melt, extract by boiling with a 5 per cent. solution of sodium carbonate, and filter.

<table>
<tr><td colspan="2">Residue. Boil with dilute nitric acid, filter and wash the residue.</td><td colspan="3" rowspan="2">Filtrate. Acidify with dilute nitric acid. Boil off carbon dioxide and test the gas for hydrogen sulphide. Neutralise to litmus with ammonium hydroxide, boil and filter.</td></tr>
<tr><td rowspan="2">Residue. Dry and fuse in silica with potassium hydrogen sulphate. Leach with dilute sulphuric acid and examine for metals.</td><td rowspan="2">Filtrate. Add 2 to 3 drops of dilute hydrochloric acid, warm and filter.</td><td>Precipitate. Boil with dilute hydrochloric acid and filter.</td><td>Filtrate. Examine for anions.</td></tr>
<tr><td>Precipitate. Test for silver.</td><td rowspan="2">Filtrates. Evaporate just to dryness, take up in 2 N hydrochloric acid and examine for metals.</td><td colspan="2">Residue. Dry and fuse in silica with potassium hydrogen sulphate. Leach with a hot saturated solution of ammonium oxalate and filter.</td></tr>
<tr><td colspan="2"></td><td>Precipitate. A gelatinous precipitate of silica.</td><td>Filtrate. Add a 1 per cent. solution of tannin and examine for tantalum and niobium.[4]</td></tr>
</table>

B. Separation into groups—

Group 1—Add 2 to 3 crystals of hydrazine hydrochloride to the solution and boil until the reaction ceases. At this stage any precipitate is removed as group 1 and contains gold, selenium, tellurium and possibly platinum. This reducing treatment also breaks up chromates and vanadates; it does not break up arsenates or reduce ferric iron.

Group 2—Add several drops of concentrated hydrochloric acid to the solution and boil both to reduce the volume to 1 ml and to produce a constant-boiling acid mixture. Pass hydrogen sulphide into the boiling solution, add an equal volume of water and then 2 to 3 drops of a saturated solution of ammonium chloride to precipitate the ammonium salts of certain complex tungstic acids. Boil away the hydrogen sulphide, add as much 2 *N* ammonium hydroxide as there is liquid in the tube, boil and again pass in hydrogen sulphide; the solution will then be about 0·25 *N* with respect to hydrochloric acid. Remove the precipitated sulphides of mercury, bismuth, copper, cadmium, lead, silver, platinum, vanadium, arsenic, antimony, tin and molybdenum, thallous chloride and the ammonium salts of certain heteropoly acids of tungsten. Saturate the solution with hydrogen sulphide

and place it over a bath of boiling water for at least 15 minutes to ensure complete precipitation of all molybdenum sulphide. Remove any additional precipitate that forms on standing and include it with the main group 2 precipitate.

Group 3—Boil off hydrogen sulphide, add 1 to 2 drops of concentrated nitric acid and boil. Withdraw two small portions and test one for phosphate with nitric acid and ammonium molybdate and the other for complex tungstates with tannin as described by Holness[5]; any phosphate or tungstates present must be removed by special procedures before continuing (see under F, p. 361). Similar strictures obtain if organic radicals, fluorides, borates, and so on, are present.

When all interference is removed, withdraw a further portion and test it for iron. Add several drops of a 1 per cent. solution of ferric chloride to ensure complete precipitation of any vanadium or thallium, then add a small amount of a saturated solution of ammonium chloride and boil the solution. Add diluted ammonium hydroxide (1 + 1) dropwise to the gently boiling solution until it is just neutral to litmus, when the precipitated hydroxides and hydrated oxides of iron, manganese, chromium, aluminium, zirconium, titanium, indium, thallium, uranium, beryllium, vanadium, thorium, cerium and the rare earths are removed as group 3.

It is inadvisable to use an excess of ammonium hydroxide to precipitate this group. The presence of dissolved carbon dioxide in the ammonium solution can result in considerable precipitation of the alkaline earth metal carbonates, as well as a loss, by solution, of some uranium and rare earths. This fact is seldom commented on in works on qualitative analysis, although it usually finds mention in books on quantitative analysis.[6]

A modified procedure for group 3—Because of the possible loss, by precipitation as carbonates, of some of the alkaline earth metals in group 3 and of the tedious nature of the removal procedure when organic radicals, fluorides, borates, silicates, and so on, are present, the following alternative procedure, which can be used after phosphate and complex tungstate have been removed, has much to commend it. Add 2 to 3 drops of concentrated nitric acid, then 5 drops of concentrated sulphuric acid and evaporate until fumes of sulphur trioxide appear; on cooling, gelatinous particles of silica will be seen adhering to the sides of the beaker. Dilute with water and remove the insoluble portion, which contains silica, barium sulphate, strontium sulphate and some calcium sulphate. Oxidise the soluble portion with 1 drop of concentrated nitric acid, test for iron, add ferric chloride and precipitate group 3 as described above. Fuse the insoluble portion with sodium hydroxide as in section A above, but dissolve the precipitated carbonates in acetic acid to provide a solution for the separation of the alkaline earth metals (group 5), which can be added to that obtained by the normal method.

Groups 4, 5 *and* 6—With the exception of lithium, rubidium and caesium, only the elements usually included in the classical scheme now remain in solution. The additional alkali metals find their way into group 6, unless there is present an excess of lithium, in which event some will be precipitated in group 5 along with calcium.

C. SEPARATION OF GROUP 1—

Dissolve the precipitated elements by boiling them with a mixture of equal parts of concentrated hydrochloric acid and bromine water, boil away the excess of bromine, add an equal volume of a saturated solution of ammonium chloride and evaporate just to dryness. Leach the residue with water and remove any precipitated ammonium chloroplatinate. Boil the solution with oxalic acid to reduce to the metal any gold present; remove the metallic gold. Next add sufficient concentrated hydrochloric acid to make the solution about 2 *N* and then add 2 to 3 crystals of hydroxylamine hydrochloride; on boiling, any selenium present is precipitated. Remove the selenium and precipitate the tellurium left in solution by boiling the solution with 2 to 3 crystals of hydrazine hydrochloride.

D. SEPARATION OF GROUP 2—

Divide this group into the copper and arsenic sub-groups by heating just to boiling with an excess of the 1 per cent. lithium hydroxide and 5 per cent. potassium nitrate reagent,

as described by Holness and Trewick.[7] Separation is clean, with the sulphides of arsenic, molybdenum, antimony, tin and vanadium remaining in solution, the insoluble ammonium complex tungstates being converted into soluble lithium ones and the sulphides of the copper group being unaffected, in which form they can be removed.

The arsenic sub-group—Just acidify the filtrate from the lithium hydroxide extraction with dilute hydrochloric acid, warm, filter and wash the precipitate thoroughly with hot dilute ammonium chloride solution.

Precipitate. Add concentrated hydrochloric acid and boil. Add magnesium carbonate to expel hydrogen sulphide, dilute and filter.

Residue. Shake with a cold ammonium carbonate solution and filter.		*Filtrate.* Neutralise with ammonium hydroxide, add a large excess of oxalic acid crystals, warm, pass hydrogen sulphide and filter.	
Residue. MoS_3.	*Filtrate.* Acidify with dilute hydrochloric acid. Yellow precipitate of As_2S_3.	*Precipitate.* Test for antimony.	*Filtrate.* Add an excess of 1 per cent. tannin solution. Boil and add ammonium hydroxide dropwise until neutral to Congo Red. A white precipitate in acid medium denotes tin. A blue-black precipitate in neutral medium denotes vanadium.

Filtrate. Test for complex tungstates. Add an excess of 1 per cent. tannin solution and some ammonium chloride and boil. Add ammonium hydroxide until just alkaline to Congo Red. Boil for several minutes then make just acid with hydrochloric acid. Filter.

Precipitate. Dark brown precipitate denotes tungsten.	*Filtrate.* Destroy the excess of tannin by boiling with concentrated nitric acid, then test for silicon and phosphorus by the usual methods.

The copper sub-group—Warm the residue from the lithium hydroxide extraction with diluted nitric acid (1 + 1), dilute and filter.

Residue. Dissolve in concentrated hydrochloric acid and bromine water. Boil off the excess of bromine. Add a saturated solution of ammonium chloride and evaporate just to dryness. Extract with water and filter.

Precipitate. Yellow crystals of ammonium platinochloride.	*Filtrate.* Add dilute hydrochloric acid and stannous chloride to confirm mercury.

Filtrate. Add a few drops of concentrated sulphuric acid and evaporate until fumes of sulphur trioxide appear. Cool, dilute and filter.

Precipitate. Dissolve in ammonium acetate and test for lead.	*Filtrate.* Add concentrated hydrochloric acid and 1 drop of bromine water, and boil. Add a crystal of hydrazine hydrochloride and boil. Add a small amount of ferric chloride solution and then make ammoniacal. Boil and filter.	
	Precipitate. Dissolve in dilute nitric acid, divide into 3 portions and test separately for bismuth, thallium and vanadium.	*Filtrate.* Add 2 drops of potassium iodide solution, warm and filter.
		Precipitate. A yellow precipitate of silver iodide.
		Filtrate. Test for copper and cadmium.

E. SEPARATION OF GROUP 3—

Dissolve the ammonia precipitate in dilute hydrochloric acid, add an excess of oxalic acid, digest hot and filter.

<table>
<tr><td colspan="2">Precipitate. Cover with water; add solid ammonium oxalate. Boil, digest hot and filter.</td><td colspan="5">Filtrate. Add ammonium hydroxide to re-precipitate hydroxides, filter and wash the precipitate with a mixture of ammonium chloride and ammonium hydroxide; reject the filtrate. Dissolve the precipitate in dilute hydrochloric acid, add an excess of ammonium tartrate; make ammoniacal. Pass in hydrogen sulphide, warm and filter.</td></tr>
<tr><td>Precipitate. Cerium and rare earths.</td><td>Filtrate. Test for thorium.</td><td rowspan="3">Precipitate. Dissolve in hot dilute nitric acid. Boil off hydrogen sulphide and divide into 3 parts. Test separately for manganese, thallium and indium.</td><td colspan="4">Filtrate. Add a 5 per cent. solution of di-sodium hydrogen phosphate, warm and filter.</td></tr>
<tr><td colspan="2" rowspan="2"></td><td colspan="2">Precipitate. Add a 10 per cent. solution of sodium bicarbonate. Warm and filter.</td><td colspan="2">Filtrate. Acidify with dilute acetic acid, digest hot and filter. Ignore filtrate after first testing it for vanadium. Suspend residue in water; add solid sodium peroxide. Boil until effervescence ceases. Filter.</td></tr>
<tr><td>Precipitate. Test for beryllium.</td><td>Filtrate. Test for uranium.</td><td>Residue. Dissolve in dilute hydrochloric acid. Add solid ammonium oxalate and an excess of 1 per cent. solution of tannin. Boil and add ammonium hydroxide dropwise until neutral to Congo Red. Filter.</td><td>Filtrate. Divide into 2 portions. (1) Test for aluminium. (2) Add barium chloride solution. Filter, reject the filtrate. Boil the precipitate with dilute acetic acid and filter.</td></tr>
<tr><td colspan="4"></td><td>Precipitate. Orange complex of titanium.</td><td>Filtrate. Test for zirconium.</td><td>Precipitate. Yellow barium chromate.</td><td>Filtrate. Test for vanadium.</td></tr>
</table>

F. SPECIAL PROCEDURE FOR REMOVING PHOSPHATES AND COMPLEX TUNGSTATES—

This procedure is a simplification of the method described by Holness and Mattock[8] for phosphate removal; it effects the rapid removal of interferences from both phosphates and tungstates in one operation. Add 2 drops of a 5 per cent. aqueous solution of zirconyl chloride, 2 drops of a saturated solution of ammonium chloride, boil and add a large excess, 10 to 15 drops, of a 1 per cent. aqueous solution of tannin. To the gently boiling solution, slowly add *N* ammonium hydroxide solution dropwise until the solution is just alkaline to Congo Red, then add a further 10 drops of tannin solution and continue to boil for 3 to 4 minutes. Make slightly acid with *N* hydrochloric acid, add 5 drops of 5 per cent. cinchonine solution, boil, remove and discard the precipitated tannin complexes of zirconium (white), tungsten (brown) and tantalum (yellow); niobium (red) and titanium (orange) will also be partly removed here, but their presence should have been noted during the preliminary testing for complex tungstates.

Destroy the excess of tannin left in the solution by boiling with several drops of concentrated nitric acid or, better, by following the modified procedure described under section B above.

FEATURES OF THE PROCEDURE—

The tannin reagent—In extending the scheme of qualitative analysis to a more realistic selection of elements there is one reagent that proves to be of great importance, namely, a 1 per cent. aqueous solution of tannin. This reagent, forming as it does coloured complexes with a large number of elements, was, under the guise of "tincture of galls," a recognised reagent in qualitative analysis more than 150 years ago; yet to-day, modern textbooks make little mention of its use. As a routine preliminary test on an acid extract of the original substance its use has been described.[5] It gives clear indications and, occasionally, positive proof of the presence in an analysis of certain of the less familiar elements.

Apart from its use as a confirmatory test for tin and vanadium, its main use in the above work lies in its behaviour with the heteropoly acids of tungsten. Tungsten forms complex acids with many elements; these acids are stable in acid but not in strongly alkaline solution, although they are soluble in both media. In order to break up these complexes and identify the central complexing element, it is necessary to find a reagent that will combine with the tungsten in alkaline solution, in which the complex is unstable, and remain combined with it when the solution is acidified. Tannin does just this. By boiling it with the complex in alkaline solution the mustard-yellow tungsten - tannin complex is slowly precipitated, and this, on acidification, turns brown and remains precipitated. Hence the tungsten can be largely removed and the complexing element, frequently silicon or phosphorus, searched for in the solution by the usual tests adopted for their identification.

Acid radicals—The extension of the classical scheme described above does not affect greatly the number of acid radicals to be identified. Apart from the behaviour of tungsten, all the additional anions, such as vanadate, molybdate, selenite, selenate, tellurite and tellurate are formed from elements recognised in the systematic scheme. Hence only their initial states of oxidation need be determined for their complete identification. With tungsten present as a simple tungstate ion, this state can readily be identified, either by acidifying a neutral solution and precipitating the characteristic tungstic acid, or by using tannin in alkaline solution and then acidifying. Tungsten present as a complex is identified in the systematic scheme.

As certain of the elements dealt with in the above scheme appear in more than one of the tables of separation, the following notes are appended.

Silver—The solution for systematic analysis is essentially prepared through hydrochloric acid; consequently any silver present will be converted to silver chloride and most of it is removed as an insoluble substance, but a small amount is soluble in the acid and finds its way into group 2, where it is precipitated as silver sulphide.

Platinum—Only when selenium is present in the analysis is platinum precipitated in group 1; at other times it is precipitated as platinum sulphide in group 2. It is completely insoluble in the lithium hydroxide reagent and so finds its way into the copper sub-group of sulphides.

Vanadium—This element, reduced by hydrazine to the vanadyl state, spreads itself generously throughout groups 2 and 3. It appears in group 2 through the agency of carriers:

if no group 2 elements are present then no vanadium is found there; if members of the arsenic sub-group are present then some vanadium accompanies them; if members of the copper sub-group only are present then vanadium is found there too; if members of both sub-groups are present then vanadium is found with both members. In spite of this, some vanadium remains in solution and passes into group 3, from which it is completely precipitated only if sufficient iron is present to carry it down as hypovanadic acid. Once precipitated, it is separated along with chromium and aluminium.

Thallium—When present in the original solution in the tervalent state, thallium salts are reduced by hydrogen sulphide in group 2 and are then largely precipitated as thallous chloride. The thallous chloride still in solution passes to group 3, from which it is completely precipitated as thallic hydroxide, provided some carrier, such as iron, is present.

Complex tungstates—Each of the many elements that can form complex acids with tungsten was examined in binary mixtures under the conditions of the analysis; the following were found to do so, either wholly or partly: phosphorus, silicon, zirconium, tin, iodine, iron^{III}, titanium, platinum, tantalum and niobium. Those whose ammonium salts are insoluble or only partly soluble in hydrochloric acid are precipitated in group 2; this applies mainly to phosphotungstates and to a limited extent to silico- and zirconyl-tungstates. The remaining complexes are tested for and destroyed before group 3 is precipitated.

The chief innovations on this systematic scheme of analysis are—

(1) The introduction of a new group 1, which includes the elements selenium, tellurium, gold and platinum, by reduction with hydrazine.
(2) The treatment of silver partly as an insoluble and partly in the hydrogen sulphide group.
(3) Recognition of the formation by tungsten, during the initial stages of an analysis, of heteropoly acids.
(4) Modification of a scheme of phosphate removal to include removal of complex tungstates.

We wish to place on record our thanks to Mr. A. R. Powell for his interest in our work and for his kindly criticism of this paper during the course of its preparation.

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October 21st, 1952

The Determination of Copper with Sodium Diethyldithiocarbamate in the Presence of Nickel and Other Interfering Elements

With Particular Reference to Traces of Copper in Sodium Hydroxide

By ALAN JEWSBURY

A rapid method, not involving precipitations or filtrations, is described for determining a few parts of copper per million in the presence of several hundred parts of nickel per million. Interference from nickel is eliminated by adding an excess of ethylenediaminetetra-acetate reagent, which forms a chelate with the nickel. The excess of reagent is removed by means of magnesium sulphate solution and the copper is determined by sodium diethyldithiocarbamate. The method is applied to the determination of traces of copper in commercial sodium hydroxide and its more general application is suggested. Cobalt, manganese, iron, lead, cadmium and several other elements form similar complexes with ethylenediaminetetra-acetate and do not interfere; bismuth, mercury and silver interfere.

A METHOD for determining traces of copper in commercial sodium hydroxide was required. The main interference came from nickel, whose concentration could be as high as several hundred parts per million in samples containing only a few parts of copper per million.

In the determination of copper with sodium diethyldithiocarbamate, nickel is usually removed after precipitation with dimethylglyoxime either by filtration or centrifugation[1] or by extraction with carbon tetrachloride.[2] These methods are liable to errors from: (*i*) loss of copper adsorbed by the nickel precipitate—this is particularly large when the nickel concentration is several hundred times greater than that of the copper; (*ii*) loss of copper into the organic layer if the nickel dimethylglyoxime is extracted with carbon tetrachloride—this necessitates washing the solvent layer with ammonium hydroxide[3]; (*iii*) incomplete removal of the nickel due to the slight solubility of nickel dimethylglyoxime[4]; (*iv*) the presence of an excess of dimethylglyoxime, which can give rise to an interfering brown coloration.[5] In addition, the time required for a determination is considerably increased by the operation of filtering, centrifuging or extracting to remove the precipitate.

Scott and Russell[5] found that the nickel interference could be suppressed by increasing the ammonia concentration. Hence they were able to detect 0·1 mg of copper in the presence of 0·4 mg of nickel. But nickel has a slight interference at low copper concentrations and the extraction method cannot be used for the determination of the copper.[6]

We found that under certain conditions it is possible to produce a complex of nickel with ethylenediaminetetra-acetate that does not affect the determination of copper by sodium diethyldithiocarbamate. Subsequently, it was found that cobalt and certain other interfering elements likewise form chelates with ethylenediaminetetra-acetate, which makes direct determination of copper possible in their presence.

EXPERIMENTAL

A rapid routine method was required, so the extraction method with an organic solvent was not used. The copper complex was stabilised in aqueous solution with gum arabic, before its colour was measured on an absorptiometer.

First, a calibration graph was constructed for copper in the absence of nickel. An empty 100-ml calibrated flask and 100-ml flasks containing 1·0, 2·5, 5·0 or 10·0 ml of a standard copper solution having a copper content of 10 μg per ml were half filled with distilled water. To each flask was added 5 ml of 20 per cent. w/w citric acid solution, 10 ml of 5 *N* ammonium hydroxide solution, 2 ml of 1 per cent. gum arabic solution and 10 ml of 0·1 per cent. diethyldithiocarbamate solution, the flasks being shaken after each addition. The flasks were then filled to the marks with distilled water. The optical densities of the solutions were measured in 4-cm cells on a Spekker absorptiometer with No. 601 violet filters against a setting of 1·000

for the solution containing no copper. The drum readings were plotted against concentration of copper.

When an excess of 0·02 *N* di-sodium ethylenediaminetetra-acetate solution (EDTA) was added to a solution containing 5 mg of nickel and then all the reagents were added, as described in the preparation of the calibration graph for copper, only the faint blue colour of the nickel chelate with EDTA in ammoniacal solution was produced; the addition of the carbamate solution produced no change in colour. In the absence of the EDTA solution a similar nickel solution gave an intense yellow-green turbidity.

On attempting to develop the copper colour with carbamate solution in the presence of EDTA solution considerable interference was observed.

The time and extent of development of colour depended on the amounts of EDTA solution used (see Table I), the amount of copper present (see Table II) and the amount of EDTA solution in excess of the nickel present (see Table III).

TABLE I

EFFECT OF CONCENTRATION OF EDTA ON COLOUR DEVELOPMENT

Copper present, μg	Amount of 0·02 *N* EDTA solution added, ml	Amount of carbamate solution added, ml	Time for full colour development, minutes
50	2	20	<5
50	25	20	25

TABLE II

EFFECT OF CONCENTRATION OF COPPER ON COLOUR DEVELOPMENT

Copper present, μg	Amount of 0·02 *N* EDTA solution added, ml	Amount of carbamate solution added, ml	Time for full colour development, minutes
25	25	20	>30
50	25	20	25
75	25	20	20
100	25	20	15

TABLE III

EFFECT OF RATIO OF EDTA SOLUTION TO NICKEL

Nickel present, μg	Copper present, μg	Amount of 0·02 *N* EDTA solution added, ml	Amount of carbamate solution added, ml	Time for full colour development, minutes
nil	25	25	20	>30
10,000	25	25	20	< 5

From Table I it can be seen that an excess of EDTA retards development of the copper coloration, whilst from Table III it is evident that if EDTA is added only in slight stoicheiometric excess to the nickel, copper can be satisfactorily determined. However, this would involve prior knowledge of the amount of nickel present, and an attempt was made to eliminate interference due to the excess of EDTA solution. We found that if a solution of magnesium sulphate, equivalent to the whole of the EDTA present, was added, the copper could be determined without interference. Nickel could either be absent or be present at any concentration up to almost the equivalent amount of EDTA without interfering.

It was important, however, to have no large excess of magnesium over EDTA. If a substantial excess of magnesium was added not all of the nickel reacted with the ethylenediaminetetra-acetate and interference was again noticeable. On the other hand, a slight excess of magnesium had no effect. Thus, when 10 ml of EDTA solution, equivalent to 2·4 mg of magnesium, were used, it was safe to add up to 3·0 mg of magnesium.

We added 2·5 ml of a magnesium sulphate solution containing the equivalent of 1 mg of magnesium per ml for every 10 ml of EDTA solution used. Ten millilitres of EDTA solution are equivalent to 5·87 mg of nickel, and we found that with 10 ml of EDTA solution

and 2·5 ml of magnesium sulphate solution as much as 5 mg of nickel could be tolerated without interference in a copper determination.

It is important to add the EDTA solution before adding the magnesium. If these two reagents are added as a composite solution of the magnesium complex no chelate is formed with nickel.

Various known amounts of copper and nickel were taken and after the addition of 10·0 ml of EDTA solution and of 2·5 ml of magnesium sulphate solution, the copper coloration was developed exactly as described in the preparation of the calibration graph. Each solution was measured on a Spekker absorptiometer against a blank solution containing the same amounts of copper and nickel and all the reagents except the sodium diethyldithiocarbamate solution. This was done in order to compensate for the very pale blue of the nickel chelate in alkaline solution. The results are shown in Table IV.

TABLE IV

RECOVERY OF COPPER FROM SOLUTIONS CONTAINING NICKEL

Nickel taken, μg	Copper taken, μg	Copper found, μg	Error, μg
nil	10	9	−1
2000	10	12	+2
nil	50	49	−1
500	50	50	nil
1000	50	53	+3
2000	100	101	+1

METHOD FOR THE DETERMINATION OF COPPER IN SODIUM HYDROXIDE

REAGENTS—

Hydrochloric acid, 5 N—Dilute 430 ml of 11 *N* hydrochloric acid with water to 1 litre.

EDTA solution, 0·02 N—Dissolve 3·72 g of the crystalline dihydrate of the di-sodium salt of ethylenediaminetetra-acetic acid in water and dilute to 1 litre. Standardise the solution against a standard calcium chloride solution by the method of Betz and Noll,[7,8] using Murexide as indicator.

Magnesium sulphate reagent—A solution containing 1 mg of magnesium per ml. Dissolve 5·07 g of AnalaR magnesium sulphate, $MgSO_4.7H_2O$, and 50 g of AnalaR ammonium chloride in water and make up to 500 ml in a calibrated flask.

Citric acid solution, 20 *per cent.*

Ammonium hydroxide solution, 5 N—Dilute 280 ml of concentrated ammonium hydroxide solution, sp.gr. 0·880, with water to 1 litre.

Gum arabic solution, 1 *per cent.*—Dissolve 1 g of gum arabic in 10 ml of hot water and boil. Filter and make up to 100 ml. A few drops of thymol solution may be added as preservative.

Sodium diethyldithiocarbamate solution, 0·1 *per cent.*

PROCEDURE—

Weigh as rapidly as possible about 10 g of solid sodium hydroxide to the nearest 0·05 g. Place the sample in a tall 250-ml beaker and dissolve it in 25 ml of water. Carefully add, a little at a time, 50 ml of 5 *N* hydrochloric acid, keeping the beaker covered as far as possible with a clock glass. Boil down the solution to 50 to 60 ml and then cool it to room temperature. Add 10·0 ml of EDTA solution and 2·5 ml of magnesium sulphate solution, followed by 5 ml of citric acid solution, 10 ml of 5 *N* of ammonium hydroxide and 2 ml of gum arabic solution. Mix well after each addition. Make up to 90 ml in a graduated cylinder, mix and divide into two equal portions. To the first portion add 4 ml of sodium diethyldithiocarbamate solution, and make both portions up to 50 ml. Measure the drum reading of the first portion on an absorptiometer, using No. 601 violet filters and 4-cm cells, after setting the instrument at 1·000 for the second portion.

By reference to the calibration graph, calculate the amount of copper present.

RESULTS—

The method was applied to reagent grade and commercial sodium hydroxide containing added copper and nickel. Ten-gram samples of sodium hydroxide were dissolved in

25 ml of water, known amounts of copper and nickel were added and the copper was determined as described above. The results are shown in Tables V and VI.

TABLE V

RECOVERY OF COPPER FROM REAGENT GRADE SODIUM HYDROXIDE

Nickel added, μg	Copper added, μg	Total copper expected, μg	Copper found, μg
0	0	—	11
0	50	61	62
1000	50	61	62

TABLE VI

RECOVERY OF COPPER FROM COMMERCIAL SODIUM HYDROXIDE

Nickel added, μg	Copper added, μg	Total copper expected, μg	Copper found, μg	Error, μg
0	0	—	14	
0	50	64	64	nil
1000	0	14	13	−1
1000	50	64	66	+2
2000	0	14	13	−1
2000	50	64	66	+2

DISCUSSION

INTERFERENCE BY OTHER METALLIC IONS—

The chief interfering elements, other than nickel, in the determination of copper with diethyldithiocarbamate are cobalt, iron, manganese and bismuth, which all give coloured precipitates.

Cobalt forms chelates with EDTA in a similar way to nickel. A yellow colour is normally obtained when cobalt reacts with sodium diethyldithiocarbamate. In the presence of EDTA, 2 mg of cobalt give a very pale pink colour, which is easily compensated by a blank solution to which no carbamate has been added.

Similarly, 2-mg amounts of iron and manganese are without effect on the method. Bismuth, however, interferes because it does not form complexes with EDTA.

Several other metallic ions give a turbidity with sodium diethyldithiocarbamate.[9] The effect of the elements listed below was investigated as follows. Two milligrams of each of these elements were taken in the presence of a known amount of copper (55 μg) and, after the addition of 10·0 ml of EDTA solution and 2·5 ml of magnesium sulphate solution, the copper coloration was developed and measured as in the method previously described.

It was found that aluminium, antimony^{III}, cadmium, calcium, chromium^{III}, lead, tin and zinc do not interfere. Of these elements, lead and cadmium produce interfering white turbidities when a copper determination is attempted by the same procedure in the absence of EDTA and magnesium sulphate solution. On the other hand, it was found that mercury^{II} and silver interfere both in the presence and absence of EDTA.

It must be remembered that, if several elements that react with EDTA are present, sufficient EDTA solution should be added to combine with them all to avoid interference.

The copper coloration may be developed without the addition of the gum arabic and the extraction method with carbon tetrachloride then applied. As in the direct method, there is no interference from nickel, cobalt, iron or manganese so long as sufficient EDTA is present.

FURTHER APPLICATION—

It is possible to apply the method to large amounts of nickel by using a *N* solution of EDTA. It is then necessary to extract the copper complex with carbon tetrachloride. Hence it appears that traces of copper may be estimated in nickel and its salts. Similarly, this method would appear promising for the determination of traces of copper in the metals cobalt, iron, manganese, lead and cadmium and in their salts.

The author wishes to give thanks to Mr. R. Liptrot, A.M.C.T., who carried out much of the experimental work, to the other members of this laboratory who have also assisted, and to the Directors of Murgatroyd's Salt & Chemical Company Ltd., for permission to publish this paper.

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THE ANALYTICAL LABORATORY
MURGATROYD'S SALT & CHEMICAL CO. LTD.
ELWORTH, SANDBACH, CHESHIRE

October 16th, 1952

The Volumetric Determination of Zinc with Ferrocyanide in Magnesium Alloys

BY A. MAYER, G. BRADSHAW AND J. DEUTSCHMAN

A simple apparatus is described for the rapid and accurate determination of zinc in commercial magnesium alloys. The sample is dissolved, any copper is filtered off and the filtrate is titrated with potassium ferrocyanide, the end-point being detected by the deflection of the needle of a milliammeter connected across a pair of polarised platinum electrodes. The accuracy is better than 1 per cent.

WHEN a solution of potassium ferrocyanide is added to a zinc solution a precipitate of potassium zinc ferrocyanide, $K_2Zn_3[Fe(CN)_6]_2$, is formed. The excess of ferrocyanide at the end-point is usually detected by the change of oxidised (purple) diphenylamine sulphonate to its reduced (green) form. In spite of criticism the method is used because of its speed and simplicity, although it is necessary to control acidity, temperature and salt concentration. The method has been studied by Kolthoff and Pearson,[1] who recommend the addition of ammonium sulphate and are in favour of titrating at a somewhat elevated temperature. The recent introduction by Belcher[2] of naphthidine and its derivatives as indicators has improved this titration considerably, but it does not overcome the difficulties caused by small amounts of iron. Magnesium alloys contain 0·5 to 5 per cent. of zinc and up to 0·04 per cent. of iron. This amount of iron is not enough to make a significant difference to the zinc result, but it leads to the formation of Prussian blue, which obscures the end-point. The procedure now suggested overcomes this difficulty and leads to a considerable saving in time, for it obviates the necessity of carrying out a zinc sulphide separation.

The dead-stop end-point method has been described by Foulk and Bawden[3] in 1926 and has been applied by Swinehart for the titration of zinc with ferrocyanide.[4] With the aid of a Cambridge electro-titration apparatus we have found that the method as described by Swinehart is capable of giving accurate results but, owing to the long period of the galvanometer, more than half the titration time is required to allow the galvanometer to come to rest. Swinehart used a polarisation potential of 0·2 volt with small electrodes, so he had to use a sensitive detecting device. By increasing the size of the electrodes and applying a potential of 0·8 volt it has been found possible to use a milliammeter. The needle of this remains close to zero during the titration and then shows a marked permanent deflection at the end-point, which is caused by depolarisation of the anode by the excess of ferrocyanide. The theoretical considerations involved in this method of end-point detection have been

debated for a considerable time, but no suggestion so far put forward accounts for all the observed facts. The most recent work by Stone and Scholten[5] suggests electrolytic oxidation at the anode and reduction at the cathode as the probable mechanism. These authors conclude that any system, which changes from an electrolytic redox couple to but one process, or *vice versa*, at the equivalence point, can be titrated.

Experimental

Apparatus—

The apparatus was constructed from standard radio components. The complete apparatus is fitted with a motor-driven glass stirrer, a small hot-plate and an automatic burette. Details of the wiring are shown in Fig. 1.

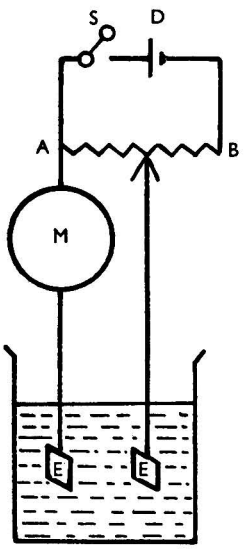

Fig. 1. The electrotitration circuit. AB, wire-wound radio-type potentiometer (200 Ω); D, dry cell (1·5 V); E, platinum foil electrodes (2·5 cm square); M, milliammeter (0 to 1 mA scale, resistance about 100 Ω); S, single pole on - off switch

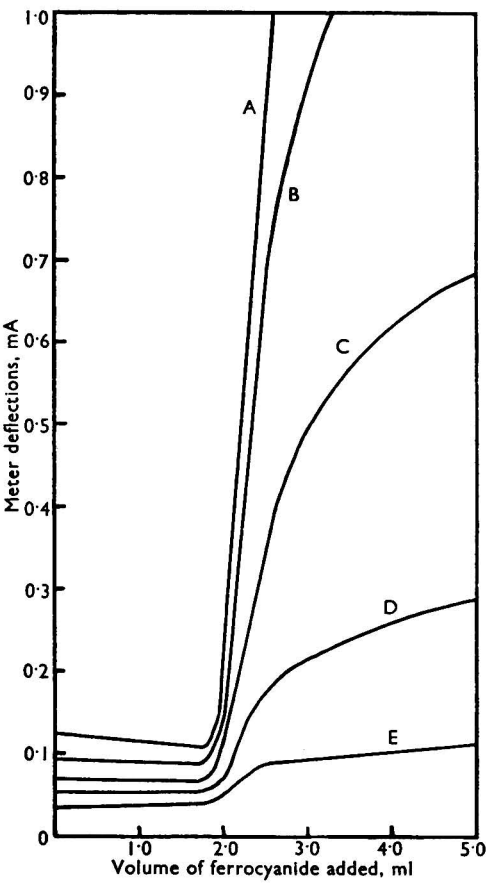

Fig. 2. Effect of polarisation potential. Potentials applied: curve A, 1·0 V; curve B, 0·8 V; curve C, 0·6 V; curve D, 0·4 V; curve E, 0·2 V

As the polarisation potential need not be critically adjusted, a rough calibration of the potentiometer is sufficient. This is best carried out by means of a valve voltmeter connected across the electrodes or with an ordinary voltmeter of high resistance. In the latter method it is desirable to replace the milliammeter temporarily with a resistance equal to that of the meter to avoid overloading it.

Choice of electrodes and meter—

To attain the best sensitivity for the detection of the end-point, the surface area of the electrodes should be balanced against the range of the meter used. One apparatus in use

in our laboratory consists of 2·5-cm squares of platinum foil mounted on stout platinum rods used in conjunction with a milliammeter (range 0 to 1 mA) of 100 ohms resistance. The sensitivity of this apparatus is such that an 0·1-ml excess of ferrocyanide causes a permanent deflection of about 0·1 mA when the electrodes are polarised to 0·8 volt. A similar sensitivity can be achieved with spiral electrodes made from 24 S.W.G. platinum wire, 52 cm long. A second apparatus in use consists of 2·5-cm lengths of platinum wire, 24 S.W.G. in conjunction with a microammeter of range 0 to 50 μA, or 5-cm lengths of the same wire with a meter having a range of 0 to 100 μA. The distance between the electrodes is not critical and in various assemblies we have used electrodes spaced between 2 and 10 cm apart.

Standard zinc solution was prepared by dissolving pure zinc in dilute sulphuric acid to make a solution containing 5·0 mg of zinc per ml. Potassium ferrocyanide solution was prepared by dissolving 21·6 g in 1 litre of water. The solution was standardised and adjusted so that 1 ml was equivalent to 5·0 mg of zinc.

THE EFFECT OF POLARISATION POTENTIAL—

This was investigated by titrating 25 mg of zinc in about 300 ml of solution containing 5 ml of concentrated sulphuric acid, and applying various voltages by means of the potentiometer. The results, shown in Fig. 2, are plotted as volumes of ferrocyanide against meter deflections in milliamperes at various applied potentials. It is evident that the position of the end-point is unaffected by the applied potential. An increase of potential increases the sensitivity. We prefer to use about 0·8 volt for the titration. Higher potentials cause excessive oscillations of the meter needle during the titration and little extra sensitivity is gained. The ferrocyanide is best added as far away as possible from the anode so as to avoid oscillations during the addition.

THE EFFECT OF TEMPERATURE—

Below 60° C the titration is slow and the end-point is not clearly defined. It is our practice to boil solutions for 5 minutes after filtration and to titrate at 65° to 95° C. The 5-minute boiling period removes dissolved hydrogen from the solution. If hydrogen is not removed it causes depolarisation and gives rise to a high residual current.

THE EFFECT OF ACIDITY—

Additions of 5 to 25 ml of concentrated sulphuric acid to a volume of 300 ml of solution made no difference in the results. Greater additions of acid caused slightly lower results.

THE EFFECT OF FERRICYANIDE—

If small amounts of ferricyanide are added to the solution, the sensitivity shows a marked increase. Ten milligrams of potassium ferricyanide were found to be the optimum amount. Ferricyanide also gives rise to a high initial residual current, which gradually drops during the titration and reaches a minimum value at the end-point (see Fig. 3). On the whole there is little to be gained by the addition of ferricyanide; since it involves an extra reagent it is not used in the procedure now proposed.

THE EFFECT OF AMMONIUM SULPHATE—

Kolthoff and Pearson[1] and Swinehart[4] recommend addition of ammonium sulphate to sharpen the end-point. With the apparatus described, the addition of up to 5 g per 300 ml of ammonium sulphate made no difference to the end-point.

THE EFFECT OF ANIONS—

Sulphate, chloride, fluoride, phosphate and perchlorate do not interfere. One gram of silica as sodium silicate made no difference to the results. Large amounts of nitrate cause low and erratic results. The amount of nitrate that can be tolerated depends on the temperature. At 60° to 70° C, 2 ml of 14 *N* nitric acid in 300 ml of solution caused no interference, but at 95° C as little as 0·25 ml has caused slightly low results. The addition of urea when nitric acid is present improves the results slightly, but it is not safe to exceed a concentration of 2 ml of 14 *N* acid at 70° C.

Nitrite acts as a depolariser, but its interference can be suppressed readily by the addition of urea. Permanganate causes high results and should be reduced by adding a slight excess of nitrite and urea. Permanganate may be present as the result of oxidation during a

preliminary electrolytic removal of an element such as copper. One gram of oxalate per 300 ml of solution causes no interference.

THE EFFECT OF CATIONS—

The following cations do not interfere: 10 g of magnesium; 1 g of lithium, sodium, potassium, lead or barium; 0·5 g of rare earth metals (Mischmetall type), zirconium, thorium; or 0·1 g of manganese or calcium.

Copper—Copper forms a brown precipitate with ferrocyanide and must therefore be absent. When magnesium alloys are dissolved in sulphuric acid, most of the copper remains

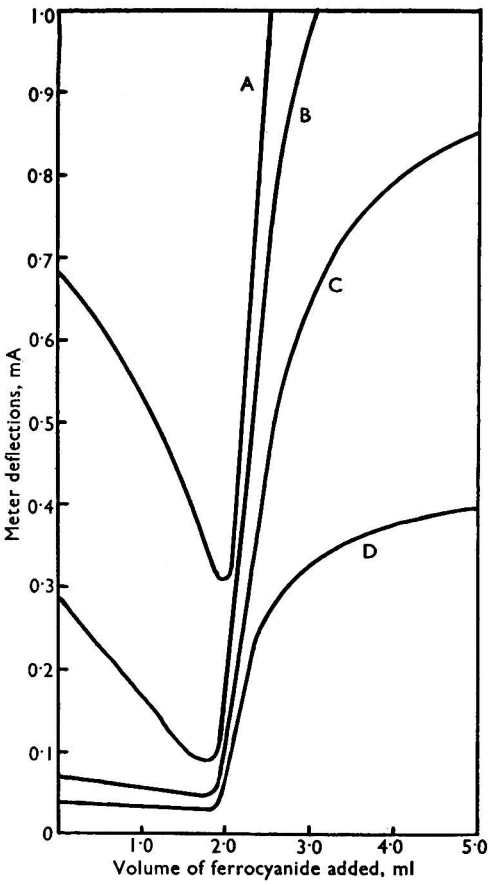

Fig. 3. Increased sensitivity with 10 mg of potassium ferricyanide added. Polarisation potentials applied: curve A, 0·8 V; curve B, 0·6 V; curve C, 0·4 V; curve D, 0·2 V

insoluble. If the solution is filtered immediately, the amount of dissolved copper is too small to make any difference in the zinc titration. For example, a sample containing 5·7 mg of copper was dissolved; the solution contained 0·6 mg of copper on filtering immediately, and 0·75 mg after setting it aside for 15 minutes before filtration. If for some reason the copper content of the solution is excessively high it may be removed by electrolysis with platinum electrodes or by precipitation as copper sulphide.

Aluminium—In the presence of aluminium the end-point of the titration cannot be detected readily. Interference can be overcome by the addition of potassium fluoride; 10 ml of potassium fluoride solution (300 g per litre) is sufficient for each 0·4 g of aluminium.

Iron—Ferrous iron acts as a depolariser and causes a high residual current. If the iron is oxidised with nitric acid, the residual current becomes less but is still higher than is normal. A mixture of iron ferrocyanides is co-precipitated with zinc and causes high results.

Magnesium alloys do not usually contain more than 0·04 per cent. of iron and in most alloys the amount is too small to make an appreciable error in the zinc figure. In the presence of 2 to 5 mg of iron^{III} the addition of potassium fluoride reduces the rather high residual current. It is possible to correct for up to 5 mg of iron, whether fluoride is added or not, by deducting 0·7 mg of zinc for every 1 mg of iron present. If more than 5 mg of iron is present, the results are erratic and it is necessary to carry out a separation; precipitation of zinc sulphide from a citrate-buffered solution is satisfactory.

Tin—Tin^{II} acts as a depolariser; tin^{IV} causes high results. In the presence of 10 ml of potassium fluoride (300 g per litre) up to 25 mg of tin^{IV} is tolerated; larger amounts cause high results, and must be removed. The separation of tin can be carried out readily by treatment with hydrogen sulphide. Adjust the acidity of the solution so that it contains about 5 ml of 5 *N* sulphuric acid per 200 ml, heat to boiling and pass hydrogen sulphide until the solution is cold. Filter through a pad, wash with dilute sulphuric acid saturated with hydrogen sulphide and boil the filtrate until free from hydrogen sulphide. Add a few drops of nitric acid and boil for a few minutes before titrating. A sample containing 17 per cent. of tin, to which was added 3·00 per cent. of zinc, was dissolved and the tin removed by precipitation as sulphide. The zinc found was 3·02, 3·02 per cent.

Cadmium—Under the conditions specified in the procedure large amounts of cadmium cause the equilibrium at the end-point to be established slowly and the results are slightly high. This is probably due to co-precipitation. When an alloy containing 3·30 per cent. of zinc, to which had been added various amounts of cadmium, was titrated, the following results were obtained—

Cadmium added, per cent.	0	3·3	6·7	10·0
Zinc found, per cent.	3·30	3·34	3·37	3·42

If necessary, cadmium can be removed by electrolysis of the filtered solution after adjusting the acidity so that the solution contains 10 ml of 5 *N* sulphuric acid per 200 ml, adding 0·01 g of gelatin and electrolysing with copper-coated platinum electrodes as recommended by Osborn.[6]

Nickel and cobalt—Magnesium alloys do not usually contain more than 0·01 per cent. of nickel or cobalt and this amount causes no interference. More than about 4 mg cause high results. To an alloy containing 3·00 per cent. of zinc was added 10 and 25 mg of nickel; 3·03 and 3·06 per cent. of zinc, respectively, was found.

Silver—Silver interferes by causing high results. Thus, when to an alloy containing 3·00 per cent. of zinc was added 50 and 100 mg of silver, 3·31 and 3·58 per cent. of zinc, respectively, was found. The addition of sufficient chloride ions to precipitate all the silver overcomes this interference. It is not necessary to remove the precipitate of silver chloride.

Titanium—Titanium is not normally present in magnesium alloys, but it is of interest to compare its effect with that of zirconium and thorium, which do not interfere. Titanium^{III} acts as a depolariser and must be absent. It can be oxidised to titanium^{IV} by addition of permanganate, followed by sufficient nitrite to reduce the excess, and the addition of urea to remove the excess of nitrite. When large amounts of titanium^{IV} are present the results are high and pale brown titanium ferrocyanide is precipitated. The interference of titanium can be largely suppressed by the addition of potassium fluoride. To an alloy containing 3·00 per cent. of zinc various amounts of titanium were added with the following results—

Titanium added, per cent.	1·7	8·5	8·5
Potassium fluoride solution (300 g per litre), ml ..	10·0	—	10·0
Zinc found, per cent.	3·02	3·16,3·11	3·05,3·05

Thallium—Thallium^{III} acts as a depolariser. Thallium^{I} gives rise to slightly high results. Thus, the addition of 0·5 g of thallium^{I} to a sample containing 3·00 per cent. of zinc caused an increase to 3·03 per cent.

Thallium, titanium and cobalt are not commonly found in magnesium alloys; they were studied on account of their theoretical interest.

Silver and tin have been specified as constituents of magnesium alloys, but their use is rare.

THE REMOVAL OF INTERFERING ELEMENTS WITH HYDROGEN SULPHIDE—

When hydrogen sulphide has been used to remove elements like copper or tin, the filtrate must be boiled until it is free from hydrogen sulphide. Any remaining polysulphides would give rise to a high residual current and must be removed. This is best achieved by oxidation with a few drops of nitric acid.

METHOD

REAGENTS—

Sulphuric acid—The concentrated acid.

Potassium ferrocyanide solution—Dissolve 21·6 g of pure $K_4Fe(CN)_6.3H_2O$ in water and dilute to 1 litre.

Potassium fluoride solution—Dissolve 300 g in water and dilute to 1 litre.

PROCEDURE—

Weigh accurately 2 to 6 g of sample (Note 1), transfer to a 400-ml beaker, cover with 100 ml of water, add 3 ml of concentrated sulphuric acid per gram of sample plus 5 ml in excess and allow the alloy to dissolve (Note 2). Boil for 5 minutes to remove dissolved hydrogen (Note 3). Dilute to about 300 ml with hot water and adjust the temperature to between 60° and 70° C. If aluminium, small amounts of tin or between 2 and 5 mg of iron are present, add 10 ml of potassium fluoride solution (Note 4). Set the polarising voltage to 0·8 volt; the milliammeter should now read 0·05 to 0·15 mA. Titrate with standardised ferrocyanide solution until the meter shows a permanent deflection. Ample warning of the approach of the end-point is given by the needle oscillating and returning to its original position. At the end-point it is advisable to add 0·1 ml of ferrocyanide solution in excess; the needle should then show a further permanent deflection of about 0·1 mA.

STANDARDISATION OF THE FERROCYANIDE SOLUTION—

Standard zinc solution—Dissolve 5·00 g of pure zinc in dilute sulphuric acid and dilute to 1 litre (1 ml is equivalent to 0·0050 g of zinc). By means of a pipette transfer 25 ml of this solution to a beaker, add 5 ml of sulphuric acid, dilute to about 300 ml with hot water, and titrate with ferrocyanide.

NOTES—

1. The weight of sample should be adjusted according to the zinc content. For 0·5 to 2 per cent. of zinc take 6 g of sample, for 2 to 4 per cent. of zinc take 3 g of sample, for 4 to 8 per cent. of zinc take 2 g of sample.

2. If more than 0·01 per cent. of copper is present, filter immediately after solution is complete. Large amounts of cadmium should be removed by electrolysis. If more than 25 mg of tin is present, carry out a hydrogen sulphide separation.

3. If small amounts of tin^{II} or between 2 and 5 mg of iron are present, add dropwise approximately 0·1 *N* potassium permanganate solution until the pink colour persists, reduce the excess with a few drops of sodium nitrite solution (10 g per litre) and add about 0·5 g of urea.

4. Most brands of potassium fluoride cause a slight blank error, usually equivalent to about 0·1 ml of ferrocyanide; this is probably due to impurities. It is necessary, therefore, to carry out the standardisation with and without the addition of potassium fluoride and to make allowance for the blank error.

5. The electrodes should be cleaned frequently by dipping first in sodium hydroxide solution (approximately 10 per cent.) and then in nitric acid (approximately 4 *N*). To avoid damaging the meter, no polarising voltage should be applied during cleaning.

RESULTS—

The method described has been in routine use for several months and the results have been in excellent agreement with those of other methods. To test the reproducibility, a sample of magnesium - zirconium - zinc alloy was analysed by seven assistants, each carrying out four determinations over a period of 2 weeks. The average was 4·80 per cent. of zinc and the maximum deviations from the mean for the determinations were +0·03 and −0·015 per cent. of zinc. The standard deviation was calculated to be 0·011 or 0·23 per cent.

OTHER APPLICATIONS OF TITRATIONS WITH POLARISED PLATINUM ELECTRODES—

In hot, neutral solutions containing 50 per cent. by volume of alcohol, Mischmetall-type rare earths can be titrated with ferrocyanide; the end-point is not as sharp as in the titration of zinc, but can be detected readily. It has not been found possible to titrate calcium with ferrocyanide, either in aqueous or 50 per cent. alcoholic neutral solutions. The apparatus described can be used satisfactorily for the titration of acid by alkali with hydrogen peroxide as the depolariser; for the titration of chloride with silver nitrate in neutral solution with nitrite as the depolariser; and for the titration of iodide with silver nitrate in which the iodide acts as the depolariser. The titration of these systems has been suggested by Clippinger and Foulk.[7]

The authors wish to thank the Chairman and Directors of Magnesium Elektron Limited, Clifton Junction, Manchester, for permission to publish this paper.

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MAGNESIUM ELEKTRON LIMITED
CLIFTON JUNCTION
MANCHESTER

October 31st, 1952

A Research Polarograph for Photographic Recording and a Multipurpose Polarographic Cell

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The circuit lay-out and operation of a photographically-recording polarograph are described. Incorporated in the instrument is an auxiliary potentiometer, which allows the change of applied potential per unit division of the polarogram to be varied for any required starting potential. There is also variable galvanometer damping and "forward" and "reverse" operation of the potentiometer drive; either of two rates of potential change can be applied to the cell. In addition, a lamp circuit is included, which may be used in marking the photographic record at any point when recording the polarogram. Two polarograms are discussed in detail in order to illustrate the application of the instrument to polarographic problems.

A multipurpose polarographic cell, which allows determination of the pH of the solution and of m and t for the electrode without removal of the solution from the cell, is also described.

IN previous work on traces (μg per ml) of easily reducible ions such as uranium^{VI}, it was found that the accuracy with which the step-heights could be measured was considerably improved by working with a total voltage of only 0·5 volt applied across the ends of the main potentiometer of a Cambridge polarograph, instead of with the 3·0 volts specified by the manufacturers. This reduction of voltage resulted in an "extension" of the polarographic wave over the photographic record producing a more clearly defined step. With this technique, steps 2 to 3 mm in height (on maximum sensitivity), which were barely detectable and entirely unmeasurable under normal conditions, were easily measured (see also Werthessen and Baker.[1])

The circuits of the Cambridge photographic-recording polarograph and of similar instruments constructed in this laboratory are such that the amount by which the wave can be "extended" decreases as the half-wave potential of the step to be measured becomes more negative; the technique cannot be applied satisfactorily to the determination of elements

of half-wave potential greater than about −0·5 volt measured against the saturated calomel electrode.

The modification of an existing polarograph was considered impracticable, so it was decided to build an instrument for which the magnitude of the potential change across the cell electrodes per unit distance on the polarogram could be varied for any required starting

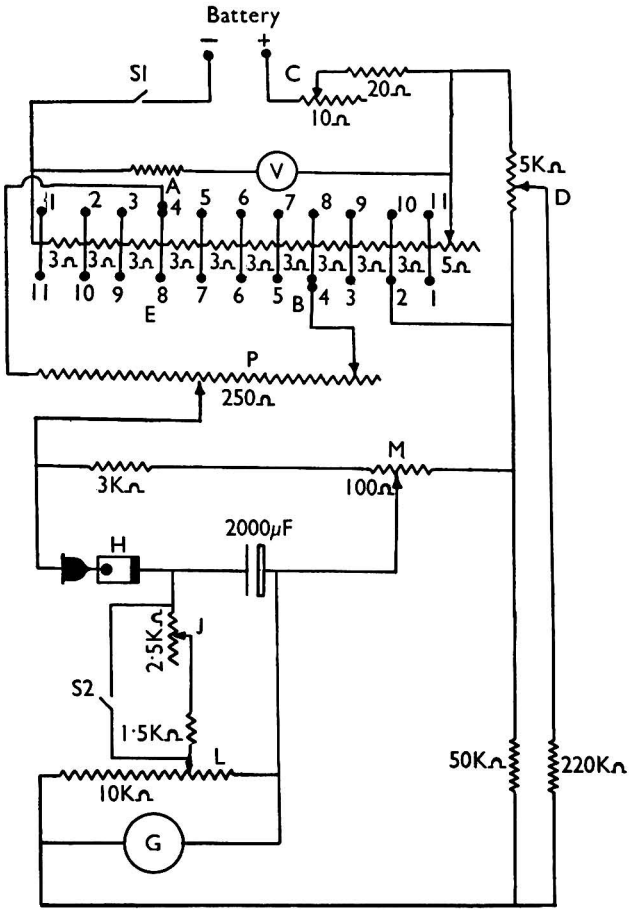

Fig. 1. Circuit diagram. A and B, tappings; S1, battery switch; S2, damping switch; C, voltage control; V, voltmeter; D, zero-adjustment control; E, potential selector; G, galvanometer; H, polarographic cell; J, damping control; L, sensitivity control; M, counter-current control; P, main potentiometer

potential. Other refinements for making the instrument more suitable for fundamental investigations involving the accurate determinations of half-wave potential and electron transfer included—

(1) "Normal" and "slow-speed" operation of the potentiometer drive.

(2) Variable galvanometer damping.

(3) Devices for selecting a suitable starting potential and for varying the potential scale on the photographic record.

(4) "Forward" and "reverse" operation of the potentiometer drive.

(5) A method of marking the photographic record at any instant during the recording of a polarogram.

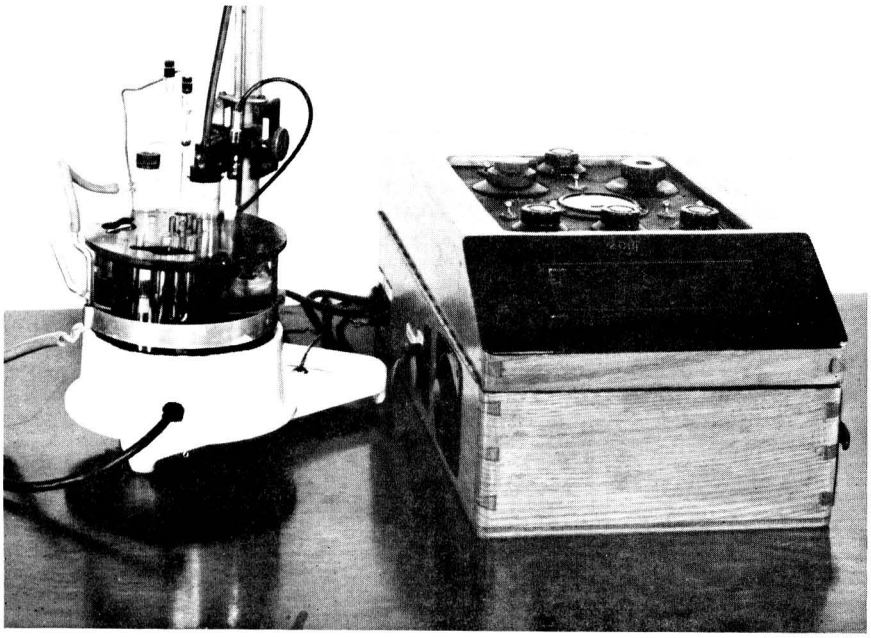

Fig. 2. General view of the research polarograph and multipurpose cell

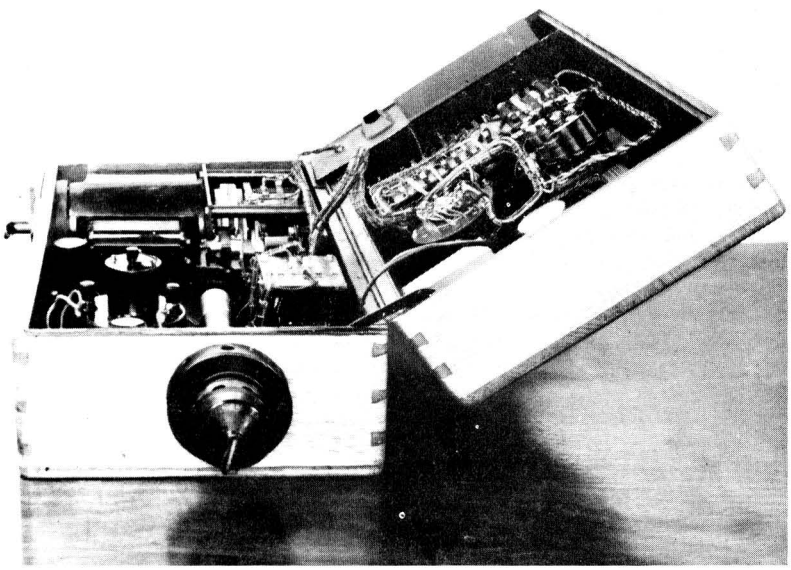

Fig. 3. Internal arrangement of the research polarograph

A number of these refinements are incorporated in the Cambridge photographic-recording and direct-writing polarographs, but neither instrument contains all of them. Those in our polarograph are either of simpler operation or more comprehensive.

We required for use with this polarograph a multipurpose cell incorporating a means of measuring the pH of the solution and m and t for the dropping-mercury electrode without removing the solution from the cell. It was also desirable that the size and shape of the cell

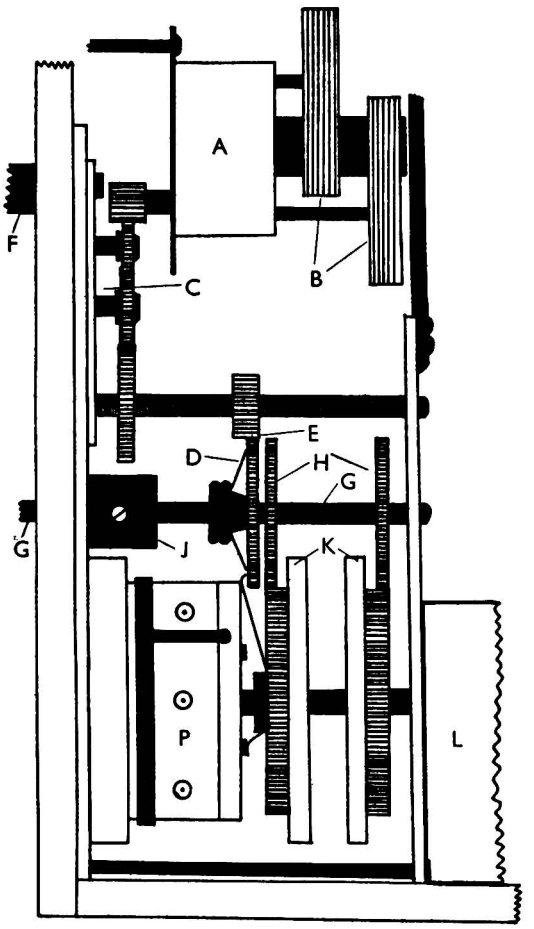

Fig. 4. Motor and potentiometer unit. A, motor; B, field coils; C, gear box; D, friction drive; E, reduction gear; F, gear-plate position control; G, main spindle; H, main drive wheels; J, re-setting plunger block; K, pointer; L, camera drum; P, potentiometer

should be such that it could be used in a Cambridge thermostat bath of substantially unmodified design. A large number of specially designed cells are described in the literature, of which typical examples are those produced by Smith.[2,3] These were too complicated for our purpose and also had the disadvantage of requiring specially constructed thermostat baths. As an alternative to the modification of existing designs an entirely new cell was designed.

Description of the Polarograph

General construction—

This polarograph, the circuit of which is shown in Fig. 1, is similar in general lay-out to the Cambridge photographic polarograph; a number of standard Cambridge components

were used in its construction. A general view of the instrument is shown in Fig. 2 and its internal arrangement can be seen from Fig. 3.

The motive power for the potentiometer and camera drum is provided by a synchronous motor via a reduction gear and friction drive. The details of this unit are given in Fig. 4. The motor, A, is a "Synclock" type CX, operated by 230-volt 50-cycle A.C. mains. This motor is provided with two field coils, B, which control its direction of operation. Selection of the direction of movement of the potentiometer and camera drum is made by means of a switch, which brings one or other field coil into circuit.

"Normal" and "slow-speed" operation of the instrument is attained by interposing a gear-box, C, between the motor and the friction drive, D, and reduction gear, E. This gear-box, shown in detail in Fig. 5, is constructed on a swivelling metal plate, which can be rotated to lock either of the two gear trains in mesh. In the "normal" position a ratio of

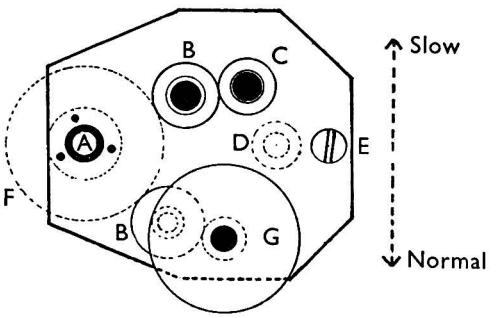

Fig. 5. Gear plate. A, brass bush; B, drive with 36 teeth; C, drive with 23 teeth; D, drive from motor (25 teeth); E, gear lever; F, drive for potentiometer and camera; G, double-drive with 20 and 75 teeth

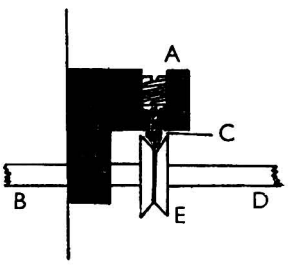

Fig. 6. Re-setting device A, adjusting screw; B, manual control; C, spring-loaded plunger; D, Spindle of potentiometer drive-wheel; E, V-grooved wheel

approximately 1:1 is engaged, giving a time for total rotation of the potentiometer arm, and camera drum of 11 minutes. In the "slow" position an approximately 4:1 ratio is engaged so that the time for total rotation becomes 45 minutes. The position of the gear plate is controlled by a knob, F, on a threaded spindle, which moves in a vertical direction in a slot. In the down position speed is "normal" and in the up position the instrument is set for "slow" rotation. Between these there is a "neutral" position. The selected gear is locked in mesh by rotating the knob, F, on its spindle until it is tight against the slotted plate. The knob and slotted plate are visible on the left-hand side of the instrument in Fig. 2.

Manual movement of the potentiometer and camera drum is effected by means of a second knob also visible in Fig. 2, which is connected to the main spindle, G. Separate manual rotation of either the potentiometer or camera drum is effected by sliding the main spindle until one of the main drive wheels, H, is disengaged. This spindle is moved by pushing in or pulling out the manual-control knob. The spindle is maintained in a central position by means of a V-grooved wheel and re-setting plunger mounted in a block, J. This device is shown in Fig. 6. The degree of rotation of the potentiometer is shown on engraved drums, K, by means of a pointer.

The current flowing through the polarographic cell enters the instrument via a jack and plug on the left of the instrument (Fig. 2) and is measured with a Cambridge D'Arsonval long-period galvanometer, which has a variable shunt incorporated in its circuit (Fig. 1). The optical systems used for recording the movement of the galvanometer and ruling the background photographically are, in general, the same as the system used in the Cambridge polarograph[4] and the projector lamp and camera are standard Cambridge components. A Cambridge-type Safelight is also included, so that the scale can be viewed without the camera being affected.

Over-exposure of the photographic record on "slow-speed" is avoided by filters, which fit over the projector lamp and over the lamp used for ruling the polarogram (the "ground-light").

The circuit of the Safelight is interrupted by a jack, which is normally kept short-circuited. When it is desired to mark the polarogram at particular points the short-circuiting jack is removed and replaced by one connected by a flex to a push-button switch. Then by use of the Safelight with its filter removed, the record can be marked as is necessary, such as at absolute intervals of potential determined with an external potentiometer. The mark produced on the polarogram takes the form of a heavy black line as can be seen in the polarogram shown in Fig. 7. The photographic record must have been previously exposed to the "groundlight."

The polarograph also contains potentiometers, which control the zero position of the galvanometer spot, the amount of counter-current applied to the galvanometer and the voltage

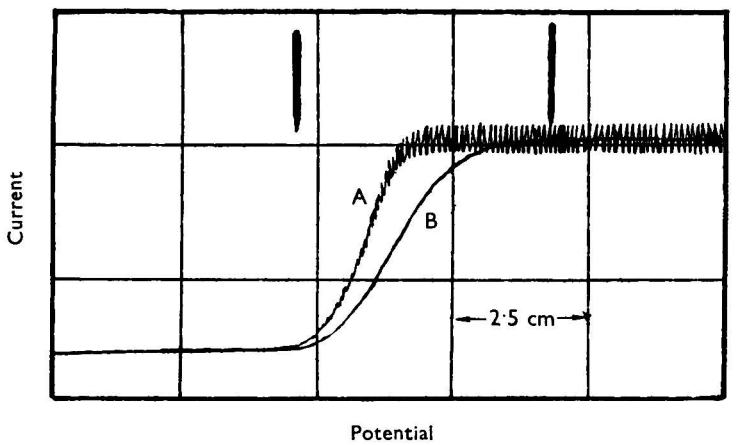

Fig. 7. Polarograms of 0·001 *M* cadmium in 0·01 *N* potassium chloride solution. Curve A, with damping control "out"; curve B, with damping control set at 3. Potential scale: 0·2 volts per cm

applied to the potentiometer circuit. The potentiometer voltage is supplied from a 6-volt accumulator connected via a plug on the left-hand side of the instrument. A voltmeter is included in this circuit to facilitate correct setting.

Details of the circuits for varying the galvanometer damping and selecting the magnitude of the potential sweep and starting potential applied by the main potentiometer are given below.

DAMPING CIRCUIT—

The galvanometer damping is controlled by a resistance - capacity circuit consisting of a 200-μF condenser and 1500 and 2500-ohm resistances in series. Provision for variation of the amount of damping applied is made by use of a variable resistor for the 2500-ohm component; in addition, a switch is provided that short circuits the resistances when it is closed. This gives an almost undamped galvanometer circuit.

THE POTENTIAL SELECTOR—

A method of selecting the potential difference applied to the ends of the main potentiometer has been provided by introducing an auxiliary potentiometer into the circuit (see Fig. 1). This component consists of two 11-contact switches with independently-operated wiper contacts mounted on concentric spindles. Ten 3-ohm wire-wound resistors are connected in series between adjacent contacts of one switch, giving a total resistance of 30 ohms. Corresponding contacts on the two switches are strapped together so that either wiper contact can be set on any one of the eleven available positions on the potentiometer.

The ends of the auxiliary potentiometer are connected to the battery supply via a variable resistance, and the voltage applied is measured by a voltmeter. The voltmeter used had a full-scale deflection of 3·2 volts and, as it was desirable to use the full-scale mark as a reference point and to have a potential difference of exactly 0·3 volt across each 3-ohm resistor, an extra 2-ohm resistance was necessary in the potentiometer circuit. This extra resistance

was provided by placing a 5-ohm variable resistance in series with the potentiometer at its positive end and connecting the positive terminal of the battery to the resistance slide contact, as shown in Fig. 1. By this means a fine adjustment of the auxiliary potentiometer was attained. This control is mounted inside the instrument and is adjusted by means of a screw slot.

The two wiper contacts on the auxiliary potentiometer are connected directly to the ends of the main potentiometer so that their relative positions control the total potential difference available for application to the polarographic cell. In addition, as can be seen in Fig. 1, the cell circuit is connected to the auxiliary potentiometer between the first and second 3-ohm resistors so that this point corresponds to zero volt across the electrodes. When the wiper contacts are set to give maximum potential difference across the main potentiometer, *i.e.*, when contacts are set at the ends of the auxiliary potentiometer, a potential change from +0·3 volt to −2·7 volts is applied to the cell during a complete rotation of the main potentiometer. This potential difference can be decreased from either end in 0·3-volt steps by moving the wiper contacts towards the centre of the auxiliary potentiometer. When they are on corresponding contacts, the ends of the main potentiometer are at the same potential and the same potential difference is applied across the cell electrodes irrespective of the setting of the main potentiometer. This arrangement can be used for amperometric titrations. Table I shows typical values of the potential sweep attainable at various settings of the potential selector.

TABLE I

POTENTIAL SWEEP

Selector settings		Starting potential, volts	Final potential, volts	Potential change on polarogram, volts per cm
on *A*	on *B*			
1	1	+0·3	−2·7	−0·20
2	1	0·0	−2·7	−0·18
4	2	−0·6	−2·4	−0·12
6	3	−1·2	−2·1	−0·06
6	5	−1·2	−1·5	−0·02
6	6	−1·2	−1·2	−0·00
6	7	−1·2	−0·9	+0·02
8	10	−1·8	0·0	+0·12
11	11	−2·7	+0·3	+0·20

NOTES—1. The settings A and B refer to the switch positions on the two contact bands of the auxiliary potentiometer.

2. The sign prefixed to the potential change in column 5 refers to the direction in which the potential of the dropping-mercury electrode is changing.

APPLICATIONS OF THE POLAROGRAPH

The application of this polarograph to each individual analytical problem will undoubtedly require a different combination of the instrumental facilities described. For this reason a list of suggested settings for various applications would be of little value and no attempt has been made to give one here. Instead, two polarograms are described in order to illustrate the use of the more important features.

CADMIUM IN 0·1 *N* POTASSIUM CHLORIDE SOLUTION—

The polarogram shown in Fig. 7 was recorded with the mercury pool as anode and with the potential selector dials set at 3 and 6, giving a cathode potential change of −0·3 volt to −1·2 volts over the 30 divisions of the polarogram, *i.e.*, 0·06 volt per cm division. The polarographic step has been recorded twice; with the damping switched out and with the damping control set at 3. It will be seen that there is little significant change in the step-height under the two conditions, but the shape of the steps are markedly different, owing to the damping lag in the second. The half-wave potential of the undamped step is −0·596 volt against the saturated calomel electrode; this is in close agreement with the published value of −0·599 volt.[5] The half-wave potential of the damped step is −0·626 volt, a difference of 0·03 volt that, although usually insignificant for analytical work, would be of importance for thermodynamic calculations.

The modification of step shape by damping may lead to serious errors when the slope of the step is used to determine the number of electrons (n) involved in the reduction of each ion. Calculation of n by means of the usual formula[6] gives a value of 1·8 electrons for the undamped wave and only 1·05 electrons for the damped step. Both steps were recorded on "normal" speed and results nearer the expected value of 2 electrons would have been obtained if "slow-speed" had been used. Further improvement could have been achieved by taking the average slope after recording the steps in the "forward" and "reverse" directions.

In addition to the intervals of potential recorded automatically on the polarogram as white (unexposed) lines, the marking device, described earlier, has been used to indicate absolute values of potential at two points on the record. These points, —0·60 volt and

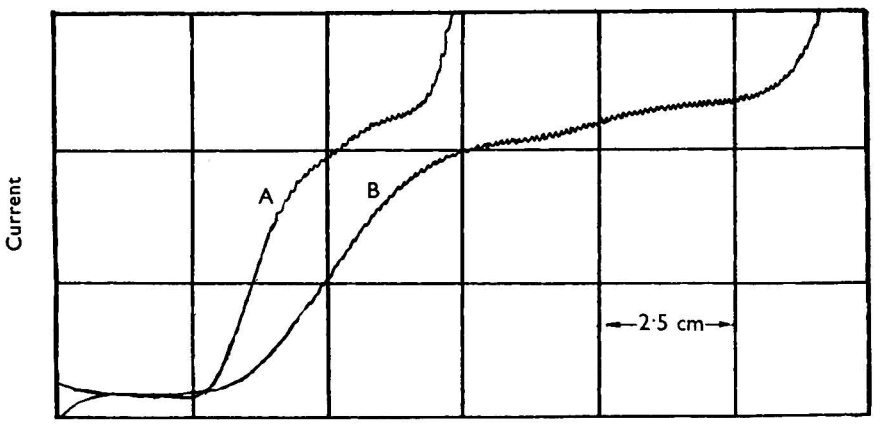

Fig. 8. Polarograms of hexavalent chromium and ferric iron in alkaline mannitol solution. Curve A, recorded with potential selector set to give a potential scale of 0·2 volt per cm; curve B, recorded with a potential scale of 0·08 volt per cm

—0·90 volt measured against the mercury pool, determined by an external potentiometer and third electrode and recorded as vertical black lines, show that the iR drop in the cell and circuit was not sufficient here to cause a significant divergence in the absolute and recorded potentials. If the difference had been significant, however, the separate recording of the positions of externally determined absolute potentials would have facilitated the correction of the indicated half-wave potentials.

IRON AND CHROMIUM IN ALKALINE MANNITOL SOLUTION—

The steps recorded on Fig. 8 are due to the reductions of hexavalent chromium and ferric iron in alkaline mannitol solution. Two records of the steps have been made at different potential-selector settings to illustrate the use of this device in separating steps occurring close together. In the first, both potential selector dials were set at 1 and the polarograph was started at 0·0 volt. This gave a change of potential of 0·0 to —2·7 volts over the first 27 divisions of the background, *i.e.*, a change of potential of 0·2 volt per cm division. This magnitude of potential change is similar to that for photographic recording polarographs.

The small step due to the ferric - mannitol complex, which follows the chromate step, is obscured to such an extent that it is unmeasurable and might not even be detected. In addition, accurate measurement of the chromate step is rendered very difficult.

The second recording was made with the potential selector dials set at 3 and 5, giving a total change of potential of —0·3 to —1·5 volts (0·08 volt per cm division). The steps appear quite separately on the record and both are measurable. In addition, accurate measurement of the small iron step has been made much easier by "extending" it over the record and, in fact, measurement is easier than it would have been on the usual voltage setting even if no chromium wave had been present.

THE MULTIPURPOSE CELL

A diagram of this cell is given in Fig. 9. Both cells are shown in position in a bath in Fig. 2. The volume of the cell is such that up to 10 ml of solution can be polarographed.

The pH of the solution in the cell is measured by inserting a Stadie-type glass electrode, A, in the ground-glass joint, B, of the cell, the calomel half-cell, C, being used as the reference electrode. When not in use the side-arm can be closed with a standard ground-glass stopper.

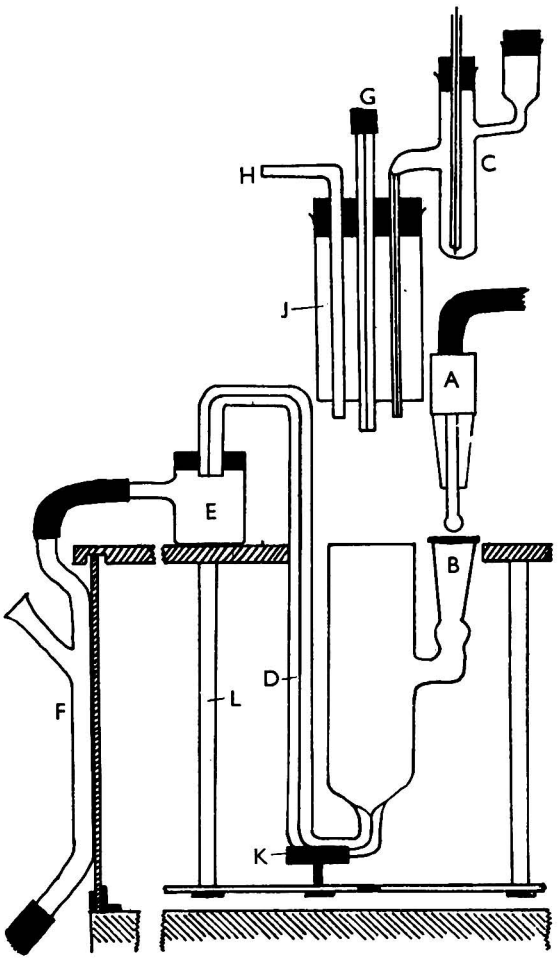

Fig. 9. Multipurpose cell. A, Stadie-type glass electrode; B, ground glass joint; C, calomel half-cell; D, capillary of 1 mm bore; E, weighing bottle; F, T-piece; G, dropping-mercury electrode; H, deoxygenating tube; J, glass sleeve; K, bracket; L, cell carrier

Electrical devices for the determination of the mass per second (m) of the mercury flowing from the dropping-mercury electrode without removal of the mercury from the cell were considered, such as those discussed by Lingane,[7] but it was decided that they offered no real advantage over the methods involving removal from the cell and weighing, provided that this could be done without loss of solution. The method adopted is similar to that described by Kolthoff and Lingane.[8] The 1-mm bore capillary, D, is of such dimensions that its upper end just enters the mouth of the weighing bottle, E, when this is standing on the cover of the thermostat bath. The side-arm of the weighing bottle is connected, via the T-piece, F, to a suction pump. The T-piece is secured to the bath by means of a metal band as shown

in Fig. 2. Suction is applied to the cell by covering the open arm of the T-piece with the thumb, and the mercury that has collected in the bottom of the cell is sucked into the weighing bottle. If the suction is discontinued as the end of the thread of mercury reaches the weighing bottle, removal of the mercury is complete, without significant loss of solution. Counting of the mercury drops is facilitated by a mirror (not shown) so set that the end of the capillary is visible from above. This mirror is mounted on the metal band that holds the T-piece in position.

The dropping-mercury electrode, G, standard half-cell, C, and deoxygenating tube, H, are inserted in a rubber bung, which also supports the glass sleeve, J, used for sealing the mouth of the cell against the atmosphere. When the mercury pool is used as the anode the half-cell is withdrawn and replaced by a glass tube with a platinum wire sealed into its lower end.

Few modifications of the thermostat bath have been necessary. The cell fits into the hole in the cover of the bath, provided that the corners of the slot, which accommodates the side-arm for the anode connector when normal type cells are used, are cut away to allow for the extra width of the ground-glass joint. The cell is supported in the bath by a small bracket, K, screwed to the cell carrier, L. These modifications do not interfere with the use of the bath for the usual type of cell, although the same dropping-mercury electrode assembly cannot be used unless the half-cell and deoxygenating table are withdrawn from the rubber bung and replaced by short glass rods.

Acknowledgment is made to the Chief Scientist, Ministry of Supply, for permission to publish this paper. The authors wish to thank Mr. R. S. Dawson for designing the gear-box and Mr. R. W. A. Hayes for wiring the polarograph.

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Chemical Inspectorate
Ministry of Supply
Royal Arsenal, Woolwich, S.E.18

September 26th, 1952

Notes

THE CHROMATOGRAPHIC SEPARATION OF POLYAMIDES

THE separation and identification of polycaproamide, polyhexamethylenediamine adipamide, polyhexamethylenediamine sebacamide (6, 66 and 610 nylons, respectively), polyurethane (Perlon U) and polyamide co-polymers can be accomplished by paper partition chromatography in which formic acid is used as the developing solvent. This procedure avoids the lengthy hydrolysis of nylon, which is a necessary preliminary to the methods developed by Haslam and Clasper,[1] and by Zahn, Wolf and Kockläuner.[2]

METHOD—

Procedure—Make 1 per cent. w/v solutions of nylons in 90 per cent. w/w AnalaR formic acid. Apply 0·025 ml of the solution to a Whatman No. 54 filter-paper by means of a micro-syringe. Form the filter-paper into a cylinder of height 11 inches and diameter approximately 2 inches, from a sheet of paper 8 inches × 11 inches, by overlapping the 11-inch sides and stitching with cotton. Develop the chromatograms (ascending method) with 88 per cent. w/w formic acid in an atmosphere saturated with water vapour at a temperature of 20° ± 2° C.

These conditions are attained by placing the cylinder of filter-paper in a dish, of diameter 3½ inches and height 2 inches, containing 30 ml of formic acid; the dish and filter-paper stand in a developing dish containing water to a depth of 1 inch and are covered with an inverted beaker, of height 12 inches and diameter 6½ inches. It is important to have sufficient water present inside the beaker to saturate the atmosphere with water vapour. If the surface area of water inside the beaker is reduced by using a beaker 5 inches in diameter instead of the larger beaker, separation is poor. The filter-paper is conditioned in the formic acid atmosphere for about 2 hours, and development takes approximately the same time. The chromatogram is dried in a current of warm air, and dyed in a 0·1 per cent. solution of Solacet Fast Blue 2BS in 0·1 per cent. acetic acid solution at 80° C for 5 minutes. The nylons can be detected as dark-blue spots. If the chromatograms are washed in hot running water for about 2 minutes after dyeing, most of the dye is removed from the filter-paper and the nylon spots are clearly visible.

TABLE I

VARIATION OF R_F VALUE WITH TYPE OF NYLON

Nylon	R_F value in 88 per cent. formic acid
6	0·8
66	0·4
610	0·3
Perlon U	0·0

TABLE II

VARIATION OF R_F VALUE WITH MOLECULAR WEIGHT OF NYLON

Nylon	Relative viscosity at 25° C	R_F value in 84 per cent. formic acid	R_F value in 88 per cent. formic acid
6	27·0	0·41	0·55
610	28·0	0·00	0·31
66	43·4	0·21	0·37
66	27·5	0·19	0·37
66	12·8	0·176	0·36

The use of other dyes, such as Naphthalene Scarlet, Methylene Blue, Solacet Fast Green, for detecting the nylon spots on the chromatogram was investigated. Solacet Fast Blue was the best of those tried, as it dyes nylon dark blue and so is readily seen.

If 90 per cent. formic acid is used to develop the chromatogram, both 6 and 66 nylons travel to the solvent front, whereas in 84 per cent. formic acid, 610 nylon does not travel at all.

R_F values are also affected by variations in molecular weight, but to a much smaller extent than by differences in type of nylon. This was clearly demonstrated by a chromatogram of 6, 610 and three 66 nylons of different molecular weights, as determined by the ratio of the absolute

viscosity of a 10 per cent. w/v solution of nylon in 90 per cent. w/w formic acid relative to that of the 90 per cent. w/w formic acid itself.

R_F values are critically dependent on the conditions of the experiment, namely, formic acid concentration, temperature and so on. Nevertheless, no special effort need be made to reproduce experimental conditions exactly, as the sequence of R_F values is always the same. This is shown by the two sets of R_F values for nylons in 88 per cent. formic acid quoted in Tables I and II. Identification can be achieved by comparing the unknown polyamide with standard polymers developed at the same time. Mechanical mixtures of polymers can be distinguished from co-polymers; the latter give single spots on the chromatogram, whereas the mixtures separate clearly into spots whose R_F values correspond to those of the individual components.

The chromatographic separations reported here are being applied to the study of "amide interchange" in polyamides.[3,4] It is often assumed that this takes place readily by the following direct mechanism—

$$[—R_1CONHR_2—] + [—R_3CONHR_4—] \rightarrow [—R_1CONHR_4—] + [—R_3CONHR_2—].$$

A comparison has been made between chromatograms of a mixture of 6, 66 and 610 polymers maintained for 2 hours at 250° C in a sealed tube, a similar mechanical mixture, and a true co-polymer of the same composition. Three distinct spots were obtained on the chromatogram of the mechanical mixture, with R_F values corresponding to 6, 66 and 610 nylon, but only one spot for both the autoclave mixture and co-polymer.

TABLE III

R_F VALUES OF A MELTED MIXTURE AND CO-POLYMER OF 6, 66 AND 610 NYLONS

Nylon	R_F value in 84 per cent. formic acid
6	0·40
66	0·31
610	0·00
Melted mixture	0·29
Co-polymer	0·37

The autoclave mixture gave a rather diffuse spot, possibly because of a wider distribution of molecular species. These results suggest that some "amide interchange," either direct or by hydrolysis and re-polymerisation, does take place at 250° C, but that true randomness has not been reached during the first 2 hours.

The author is indebted to British Nylon Spinners Ltd. for permission to publish these results.

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THE RESEARCH DEPARTMENT
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CORA W. AYERS
October 2nd, 1952

A PAPER-STRIP METHOD OF EXAMINING FUEL OILS SUSPECTED OF BEING IDENTICAL

ON numerous occasions samples of fuel oil collected from the surface of navigable waters have been submitted to us for comparison with samples of fuel oil collected from the tanks of ships suspected of having made the discharge in contravention of the Oil in Navigable Waters Act. To obtain incontrovertible evidence by the conventional methods of oil analysis that such samples are identical is almost impossible. The sample from a river has usually lost some of its more volatile constituents and, in addition, it will often be emulsified to a certain extent with water. The removal of this water by drying, filtration or solvent extraction results in a product whose analytical characteristics are significantly different from those of the original oil.

Attempts to prepare evidence of identity that could be demonstrated visually by the use of adsorbent columns and by the normal technique of paper chromatography did not produce results of the required degree of precision. The paper-strip method here described, however, gives visual evidence of complete identity or of non-identity and, if necessary, the strips can be used as evidence in a court of law (see Fig. 1).

METHOD—

Apparatus—Glass-stoppered tubes of approximately 50 ml capacity. Nessler glasses. Identical filter-paper strips 12 inches × 7/10 inch with a hole punched ¾ inch from the end of each. Suspension rod. Identical 4-oz bottles approximately 4 inches high, having necks 1¼ inches in diameter. Draught-free space, approximately 5 feet × 3½ feet × 2½ feet, which permits of ventilation. The space below an ordinary table is convenient, when suitably protected. Ultra-violet lamp.

Procedure—Transfer 1 to 3 drops of the oils to be compared to glass-stoppered tubes and add about 15 ml of ether. Rub down the oils with a glass rod, add ether to make the volume up to approximately 50 ml, shake, and set the tubes aside for 3 hours or overnight. Shake, centrifuge, filter and stopper the tubes. Dilute aliquots of each solution to the same colour intensity (approximating to that of 0·06 *N* potassium dichromate solution when viewed transversely) with the aid of Nessler glasses. Transfer exactly 50 ml to the 4-oz bottles and stopper. Press the filter-paper strips longitudinally along a thick glass rod. The slight curvature thus imparted to the strips ensures that they will hang vertically. Attach the strips to the suspension rod so that the bottom edges reach to within 2 mm of the bottom of the bottles. Make the necessary arrangements to exclude draughts and insert the strips into the bottles so that they hang freely and parallel. Complete the precautions for excluding draughts and allow the strips to remain in the ether overnight.

According to the temperature of the room, 25 to 30 ml of ether evaporate from each bottle overnight so precautions must be taken to prevent the risk of fire or explosion.

Remove the strips from the solution by raising the suspension rod, allow them to dry in air, and examine them in ultra-violet light. If the operations have been successfully carried out coloured fluorescent bands with straight edges should be observed. Normally, the desired information is obtained at this stage, but increased clarity and a greatly enhanced effect is attained by proceeding as follows.

Superimpose the strips and cut off 1 inch from their lower ends. Suspend the strips in 50 ml of ether overnight, exercising all the precautions previously taken. Remove the strips from the ether, dry them in air, and examine them in ultra-violet light; 7 to 13 fluorescent bands should be observed. For oils derived from one source these bands will be identical in colour, intensity of fluorescence, width and position on the strip. In addition they will be totally different from strips prepared at the same time from other samples of fuel oils of similar type. The accompanying photograph (taken in ultra-violet light) shows the results of the examination of four pairs of samples submitted to us. The first strip of each pair refers to the sample collected from the river or dock, and the second refers to that obtained from a ship's fuel tank.

The above procedure is an empirical method of comparison only, and it is essential that the bottles, filter-paper strips and volumes of ether solution used, should be identical. In addition, all the samples to be compared should be treated in the same place and at the same time.

The method, although originally applied to fuel oils, has been used to prove the identity of samples of tar withdrawn from a sewer at different manholes over a distance of several miles; it has permitted comparison of these samples with a small specimen obtained near the premises suspected of having been responsible for the discharge.

I am grateful to the Scientific Bureau, City of Glasgow Police, who prepared the ultra-violet light photograph.

CORPORATION CHEMIST'S AND CITY ANALYST'S DEPARTMENT
20, TRONGATE
GLASGOW, C.1

MAGNUS HERD
October 2nd, 1952

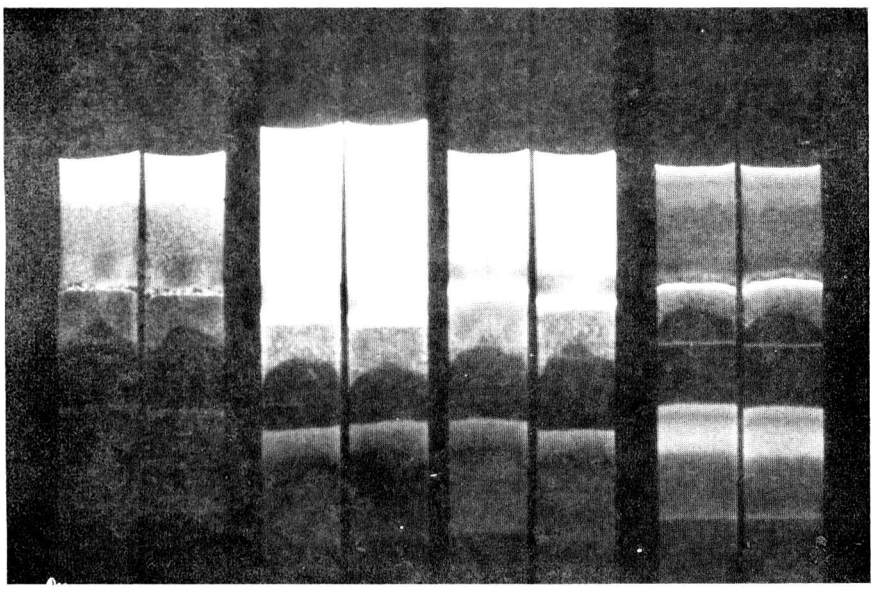

Fig. 1. Comparison strips obtained from the examination of four pairs of fuel oils

DETERMINATION OF GOLD IN SOLUTION BY ADSORPTION EXTRACTION AND SPECTROGRAPHY

GOLD extraction by adsorption on ethyl cellulose[1] has been found to be applicable as an analytical method for the determination of gold in some acid solutions. One gram of ethyl cellulose mixed with 1 g of cellulose powder as an aid to binding, is poured dry on to a 1-g layer of cellulose powder in a $\frac{3}{4}$-inch chromatography tube, and a further layer of cellulose is then poured on top. This composite pad is pressed down gently and is settled by pouring water through it. The gold solution is then poured on to the pad and allowed to seep through it; the pad is then washed four times with water. The pad is sucked dry, blown into a silica crucible, ignited at 600° C and the residue is dissolved in 1 ml of aqua regia, which is reduced in volume, by heating, to 0·75 ml and absorbed on 1 g of alumina. The resulting mixture is dried and ground with 0·1 g of a ground mixture comprised of equal parts of alumina and silver chloride containing 0·1 per cent. of added tin oxide. The tin acts as an internal standard; its quantity may be varied to suit the spectrograph. All grinding must be thorough.

The determination is carried out by carrier distillation spectrography[2,3,4] of 30 mg of the silver chloride - alumina mixture by the "two-line" method of evaluation[5,6]; the spectrum lines Au 2428·0, Sn 2421·7 and Sn 2429·5 A are used. Using various nitrating mixtures of nitric and sulphuric acids containing unknown amounts of gold and extra added gold, we have attained a mean recovery of 104 per cent. with coefficient of variation ± 5 per cent. at a mean level of 20 micrograms of gold per gram of alumina. Extractions of 4 to 50 micrograms of gold have been satisfactory from solutions containing 0·2 to 10 parts of gold per million.

We have established qualitatively that gold can be extracted from solution in either concentrated or diluted aqua regia and from solutions of chlorauric acid. Gold was not detectable in a concentrate of the stripped solution obtained from a determination with chlorauric acid.

We are indebted to Mr. R. Franklin, among others, for suggestions and assistance in the development of this method. The permission of the Chief Scientist, Ministry of Supply, to make this communication is acknowledged.

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September 30th, 1952

Apparatus

A MERCURY-CATHODE CELL FOR ELECTROLYTIC SEPARATIONS

A MERCURY-CATHODE cell of design simpler than the conventional type with an adjustable reservoir and two-way tap was required for student use in our laboratories. The apparatus proposed was constructed and has been entirely satisfactory.

The bottom of a 400-ml squat Pyrex beaker was drawn down at the centre and a system of two taps and a side-arm was joined to the centre as shown in Fig. 1. The side-arm was placed

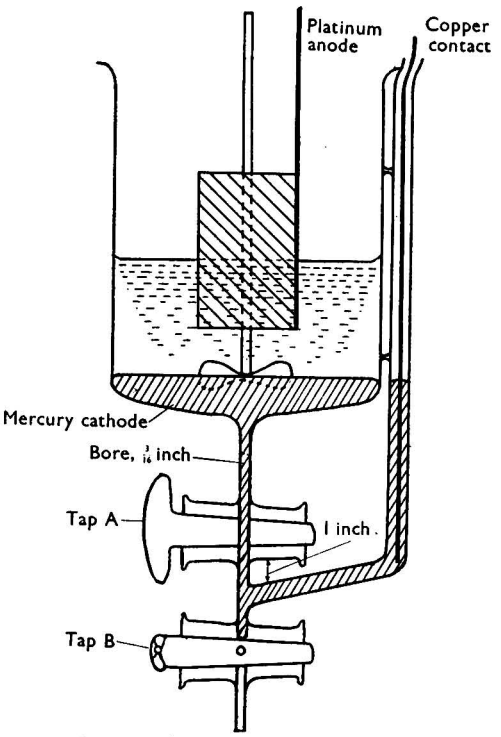

Fig. 1. The mercury-cathode cell

so that it was aligned with the side of the beaker, in which position it is less prone to fracture. Glass joints were used to fix it securely to the beaker.

Operation—With tap B closed and tap A open, the required volume of mercury is poured into the beaker. Contact with the mercury is made through the side-arm with copper wire, which passes far enough down the tube to maintain contact with the mercury when its level drops below the tap A. The solution to be analysed is then poured into the beaker. When electrolysis is complete, tap B is opened and the mercury slowly run out until the level falls about $\frac{1}{8}$ inch below tap A. Taps B and A are then closed in that order. On re-opening tap B the rest of the mercury is removed, while the small volume of solution which has passed through tap A is held in the tube by atmospheric pressure. The current is now cut off and on opening tap B the solution can be run into a separate beaker. Subsequent washing of the beaker and side-arm completes the operation. A satisfactory separation of the mercury from the solution is thus attained and subsequent filtering is unnecessary.

This apparatus has been used successfully for the past twelve months for the separation of interfering elements in samples of aluminium bronzes before an oxine precipitation of the aluminium followed by bromate titration.

DEPARTMENT OF ANALYTICAL CHEMISTRY
SCHOOL OF APPLIED CHEMISTRY
N.S.W. UNIVERSITY OF TECHNOLOGY
BROADWAY, SYDNEY
AUSTRALIA

G. H. AYLWARD
H. V. WOOLDRIDGE
September 22nd, 1952

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1953, **78**, 323).

Public Analyst	*Appointment*
ELVIDGE, William Farrand (Deputy) ..	County of Cumberland.
ELVIDGE, William Farrand (Deputy) ..	County of Durham.
ELVIDGE, William Farrand (Deputy) ..	County Borough of Carlisle.
ELVIDGE, William Farrand (Deputy) ..	County Borough of Darlington.
ELVIDGE, William Farrand (Deputy) ..	County Borough of South Shields.
ELVIDGE, William Farrand (Deputy) ..	County Borough of West Hartlepool.
ELVIDGE, William Farrand (Deputy) ..	Borough of Stockton-on-Tees.
HARRIS, Tennyson	County Borough of Wallasey.
HOUSE, Cecil John	County Borough of Bury.
SPALDING, Robert Clarence (Deputy) ..	Borough of Beckenham.
SPALDING, Robert Clarence (Deputy) ..	Borough of Bexley.
SPALDING, Robert Clarence (Deputy) ..	Borough of Bromley.
SPALDING, Robert Clarence (Deputy) ..	Borough of Chatham.
SPALDING, Robert Clarence (Deputy) ..	Borough of Dartford.
SPALDING, Robert Clarence (Deputy) ..	Borough of Tunbridge Wells.
SPALDING, Robert Clarence (Deputy) ..	Urban District of Chislehurst and Sidcup.

OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1953, **78**, 323).

Agricultural Analyst	*Appointment*
CLARK, James Frederick	County Borough of Wallasey.
ELVIDGE, William Farrand (Deputy) ..	County of Cumberland.
ELVIDGE, William Farrand (Deputy) ..	County of Durham.
ELVIDGE, William Farrand (Deputy) ..	County Borough of Darlington.
ELVIDGE, William Farrand (Deputy) ..	County Borough of South Shields.
ELVIDGE, William Farrand (Deputy) ..	County Borough of West Hartlepool.
HAMENCE, Jack Hubert	County of Wiltshire.
HARRIS, Tennyson	County Borough of Wallasey.

Ministry of Food

STATUTORY INSTRUMENT*

1953—No. 828. The Food Standards (Ice-Cream) Order, 1953. Price 2d.

This Order, which came into operation on June 1*st,* 1953, *revokes the Food Standards (Ice-Cream) (Amendment) Order,* 1952 (*S.I.,* 1952, *No.* 1283*: Analyst,* 1952, **77**, 490), *and re-enacts the Food Standards (Ice-Cream) Order,* 1951 (*S.I.,* 1951, *No.* 13*: Analyst,* 1951, **76**, 120), *restoring the standard for ice-cream to that prescribed in the* 1951 *Order.*

British Standards Institution

NEW SPECIFICATIONS†

B.S. 1921 : 1953. Dispensing Measures for Pharmaceutical Purposes (Imperial Units). Price 4s.
B.S. 1922 : 1953. Dispensing Measures for Pharmaceutical Purposes (Metric Units). Price 4s.

AMENDMENT SLIP†

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

PD 1602—Amendment No. 1 (April, 1953) to B.S. 1583 : 1950. One-mark bulb pipettes.

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.
† Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

DRAFT SPECIFICATIONS

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

Draft Specification prepared by Technical Committee LBC/1—Volumetric, Mouldblown and Lamp-blown Glassware.
CR(LBC)1446—Third Draft B.S. for Gas Washing Bottles.

Draft Specifications prepared by Technical Committee LBC/4—Thermometers.
CR(LBC)2510—Draft B.S. for Calorimeter Thermometers (Revision of B.S.791).
CR(LBC)1445—Draft B.S. for Incubator, Water Bath and Oven Thermometers for Laboratory Use (Revision of B.S.619).

Draft Specification prepared by Technical Committee LBC/11—Microchemical Apparatus.
CR(LBC)2171—Draft B.S. for Heating and Cooling Blocks for Microchemical Purposes (Part G1 of B.S.1428).

Book Review

PAPER CHROMATOGRAPHY. A LABORATORY MANUAL. By RICHARD J. BLOCK, RAYMOND LESTRANGE and GUNTER ZWEIG. Pp. x + 195. New York: Academic Press Inc. London: Academic Books Ltd. 1952. Price $4.50; 36s.

This monograph has been written to provide a readily available source of the details of a number of the uses to which paper chromatography has been put in the last few years. The authors disclaim any intention of being comprehensive, and wisely restrict themselves to putting forward matter of practical value. They claim the methods they describe to be of tried and proven worth, and to need only relatively simple equipment and available reagents; they hope that in this way they have produced a manual that will be of practical use in the ordinary chemical laboratory. They seem to have succeeded very well in their object.

They are indeed to be congratulated on choosing this method of approach to writing on the subject. The use of paper chromatography has expanded so widely in the few years it has been popular that the average worker who seeks its help needs his attention directed into the more useful channels, since he can no longer afford the time or energy for search, trial and selection. The thanks of all are due to those who can authoritatively sift out the more valuable contributions that have been made to the development of the different aspects of the subject.

The authors' choice of methods ranges over those useful for amino-acids, amines and proteins carbohydrates, aliphatic acids and steroids, purines, pyrimidines, phenols, aromatic acids and porphyrins, antibiotics and vitamins, and deals in addition with inorganic separations and the determination of miscellaneous organic substances. There is a short theoretical introduction, and a good chapter dealing with general methods and apparatus. K. A. WILLIAMS

Publications Received

PHENYLFLUORONE: REAGENT FOR GERMANIUM. By T. H. COOPER and J. T. YARDLEY, B.Sc., F.R.I.C. Pp. 8. Chadwell Heath, Essex: Hopkin & Williams Ltd. 1953. Gratis.

INORGANIC QUALITATIVE ANALYSIS. SEMI-MICRO APPARATUS AND TECHNIQUE. By H. HOLNESS, M.Sc., F.R.I.C. Pp. iv + 19. London: Sir Isaac Pitman & Sons Ltd. 1953. Price 2s.

ENCYCLOPEDIA OF CHEMICAL REACTIONS. Volume V. Edited by C. A. JACOBSON. Pp. viii + 787. New York: Reinhold Publishing Corp. London: Chapman & Hall Ltd. 1953. Price 120s.; $15.00.

Midland Society for Analytical Chemistry

IN view of the success of the short Symposium on Analytical Chemistry held in Birmingham in 1952, it is proposed to run a larger Symposium from August 25th to September 1st, 1954. This will consist of original papers and recent advances in various analytical fields.

An exhibition of new and special apparatus will be held simultaneously, and visits to local places of interest will be organised.

A ladies committee has been formed to organise entertainment for non-scientific visitors.

Further details will be made available at a later date.

Symposium Secretary—J. W. Robinson, B.Sc., Ph.D., A.R.I.C., Post Office Engineering Department, Birmingham, 9.

CHEMIST. Man of graduate standing with experience in analytical work required for analytical section of foodstuffs laboratory in Cambridge. Age under 30. Living accommodation available. Full details marked "Confidential" to Box No. 3845, THE ANALYST, 47, Gresham Street, London, E.C.2.

REQUIRED: Senior Assistant Chemist and Bacteriologist, experienced in milk and milk products testing and control. Reply stating details of age, qualifications, experience and salary required to Box No. 3844, THE ANALYST, 47, Gresham Street, London, E.C.2.

QUALIFIED ANALYTICAL CHEMISTS required for Assay Laboratory of a Northern Rhodesian Copper Mine. Starting basic salary £68 per month plus fluctuating cost of living allowance now about £7 per month. Life Assurance and Contributory Pension Scheme. Cash Bonus Scheme, which at present rate equal to 65% of basic salary. Outward passage paid. Apply giving full details of age, marital status, qualifications and experience to Box 196, Dorland Advertising, 18–20, Regent Street, London, S.W.1.

H.M. STATIONERY OFFICE: ASSISTANT EXAMINER OF PAPER AND OFFICE REQUISITES. The Civil Service Commissioners invite applications for three pensionable posts. Age limits 22–32 on 1st April, 1953, with extension for regular service in H.M. Forces and, up to two years, for established civil service. Candidates must have had such training in Chemistry and Physics as will enable them to make tests to detect faults in paper, stationers' sundries, etc., supplied for the Public Service.

Inclusive salary (London) £472 £760 (men) and £472 £628 (women); somewhat lower in Provinces. Prospects of promotion. Full particulars and application forms from Secretary, Civil Service Commission, 6, Burlington Gardens, London, W.1, quoting No. 205/53. Completed application forms must be returned by 25th June, 1953.

NATIONAL COAL BOARD—NORTH-WESTERN DIVISION

VACANCIES exist at the Central Laboratory, Shade House, Bolton Road, Pendlebury, Manchester, for the following staff:—

1. A Laboratory Assistant (male) in the Metallurgical Section. The work is principally mechanical testing and assisting in general metallurgical examination (excluding chemical analysis) of materials used in the mining industry. The minimum age limit is about 19 years, and the successful applicant will be placed in the following salary grade: Scientific Technical Officer Grade IV- 93/6 per week at 19 years rising annually to 163/- per week at 27 years of age.
2. A Laboratory Assistant (male or female) in the Analytical Section. The duties consist of general analytical work covering a wide field of materials and also research on analytical methods. Preference will be given to candidates having previous analytical experience, particularly in the field of ferrous and non-ferrous metals and the use of modern analytical technique.
   The minimum age limit is about 21 years of age and the salary grade is Scientific Technical Officer, Grade III, male £375 × £20 £535, female £300 × £16 £428 per annum. The commencing point within the scale will depend on qualifications and experience of the successful candidate.
   For this vacancy applicants should possess a Higher National Certificate or an equivalent academic qualification.

Both appointments are superannuable and candidates will be expected to undergo a medical examination.

Applications in writing, giving date of birth, qualifications, experience, etc., should be addressed to the Divisional Establishment Officer, National Coal Board, North-Western Division, 10, Portland Street, Manchester, 1, within fourteen days of the date of this advertisement.

ANALYTICAL ASSISTANT required by Pfizer Ltd. at their Folkestone Factory. Applicants should have had some experience in Pharmaceutical Analysis, and a knowledge of sterility testing is desirable. Write to Chief Control Chemist, Pfizer Ltd., Wear Bay Road, Folkestone.

ALLEN & HANBURYS LTD., Ware, Herts., require Analyst with University Degree or equivalent for work in a Physico-Chemical Laboratory engaged in the analysis of Drugs and Pharmaceutical preparations. Apply in writing giving details of age, qualifications and experience to Personnel Manager.

CHEMIST required for analytical and preparative research on inorganic chemicals and magnesium. Applicants should have B.Sc. or A.R.I.C. with some practical experience and would be expected to work under the Chief Analyst in a modern and well equipped laboratory. Salary depending on qualification and experience. Apply to the Secretary, Magnesium Elektron Limited, Clifton Junction, near Manchester.

Volume 78. No. 927, Pages 333-388 June, 1953

THE ANALYST

THE JOURNAL OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

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Printed and Published for the Society of Public Analysts and Other Analytical Chemists by W. Heffer & Sons Ltd., Cambridge, England. **Communications to be addressed to the Editor, F. L. Okell, 7-8, Idol Lane, London, E.C.3.** Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office.