THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 6 p.m. on Wednesday, February 5th, at the Chemical Society's Rooms, Burlington House, London, W.1, with the President, Dr. G. W. Monier-Williams, in the chair. The following papers were presented and discussed: "Reductometric Determination of the Sulphoxide and Amine Oxide Groups," by Mrs. Erica Glynn; "The Determination of the Composition and Constitution of Ammonium Phosphomolybdate and the Conditions affecting its Precipitation," by W. P. Thistlethwaite, B.Sc., A.R.I.C.

NEW MEMBERS

Alan Bruce Anderson, B.Sc. (Adelaide), Ph.D. (Cantab.), M.R.C.S., L.R.C.P., F.R.I.C.; Frederick George Angell, B.Sc., Ph.D. (Birm.), F.R.I.C.; Fred William Chambers, Dip.Chem. (Cologne), A.R.I.C., A.M.I.Chem.E.; Ronald Powell Graham, M.A. (Ontario), A.M., Ph.D. (N.Y.); Alexander Donovan Kenny, B.Sc. (Lond.), A.R.C.S., A.R.I.C.; Miss Muriel Meiklejohn, B.Sc., A.R.I.C.; Oswald Neave, A.R.I.C.; Neville Newsam; Arthur Stanley Nickelson, B.Sc. (Lond.), A.R.I.C.; Anthony Rhys Phillips, B.Sc., A.R.I.C.; Leonard George Sherrington, M.Sc. (Lond.), A.R.C.S.; George Arthur Colvin Sirimanne, B.Sc. (Lond.), A.R.I.C.; Frederick Lloyd Warren, M.A., B.Sc.(Oxon.), Ph.D. (Lond.).

NORTH OF ENGLAND SECTION

A MEETING of the Section was held at Manchester on Saturday, October 19th, 1946. Mr. S. E. Melling presided over an attendance of thirty. The following papers were presented and discussed: "The Determination of Traces of Lead, Zinc and Tin in Phenol," by W. Hutchinson, A.R.I.C., and H. N. Wilson, F.R.I.C.; "Soil Biochemistry," by Dr. H. Lees, B.Sc., A.R.I.C.

The twenty-second Annual General Meeting of the Section was held in Manchester on Saturday, January 25th, 1947. The Vice-Chairman, Mr. C. H. Manley, presided over an attendance of thirty-five. The Hon. Secretary presented the Report and Financial Statement, which were adopted. Appointments of Officers and Committee members for the forthcoming year were made as follows:

Chairman, C. H. Manley. *Vice-Chairman*, J. G. Sherratt. *Hon. Secretary and Treasurer*, Arnold Lees. *Committee*, R. Crosbie-Oates, A. N. Leather, R. Mallinder, Norman Strafford, G. H. Walker and H. Weatherall. *Hon. Auditors*, U. A. Coates and J. R. Walmsley.

The following paper was read and discussed: "The Chemist in the Colonies," by J. F. Clark, M.Sc., F.R.I.C.

BIOLOGICAL METHODS GROUP

The Annual Meeting of the Biological Methods Group was held in the Rooms of the Chemical Society, Burlington House, Piccadilly, W.1, at 6 p.m., on Monday, 16th December, 1946. Mr. A. L. Bacharach presided and was re-elected as Chairman. The Vice-Chairman, Hon. Sec., Hon. Auditors, and Members of the Committee also remain as last year (ANALYST, 1946, 71, 201). The Committee's Report and the Financial Statement for the period 20th February—30th November, 1946, were presented and approved. The new Rules of the Group as approved by the Council were available at the meeting in proof form.

An Ordinary Meeting of the Group followed at 6.30 p.m., at which the following papers were read and discussed: "The Assay of Anti-Thyroid Substances, using Tadpoles," by Miss H. M. Bruce (whose remarks will be embodied in a paper to appear shortly in the Proceedings of the Royal Society) and "The Computation of Microbiological Assays of Amino-Acids and other Growth Factors," by Eric C. Wood (see page 84).

The Computation of Microbiological Assays of Amino-Acids and other Growth Factors

By ERIC C. WOOD

(*Presented at the Annual General Meeting of the Biological Methods Group on December 16th, 1946*)

It is the exception rather than the rule in microbiological assays that the mean response is linearly related to the dose. Nearly all workers find this relationship to hold in the two assays most frequently required—those for riboflavine and nicotinic acid by the Snell and Strong[1] and the Snell and Wright[2] techniques respectively, or such later modifications as those described in the recent Report of this Society's Sub-Committee on Vitamin Estimations.[3] Pyridoxine assays by means of *Neurospora* may also be of this type. But assays of amino-acids and of members of the vitamin B_2 complex other than those just mentioned, usually give smooth curves, with no linear portion, when the response is plotted against the dose (for typical examples, see Barton-Wright[4]). The result of plotting the response against the logarithm of the dose, instead of against the dose itself, is usually a curve also—a disappointing result in view of the large number of biological assays in which response is linearly related to logarithm of dose. Price[5] has found this latter relationship to hold in some of his riboflavine assays and another instance is mentioned below, but in general this relationship is not found in microbiological work.

A transformation that would give linear graphs would have the advantages that the accurate computation of the best estimate of the result is made easier, and a quick visual test of validity is afforded, besides which the further calculation of the standard error and of the confidence limits of the assay, when necessary, is much simplified.

While the literature of microbiological assay is rapidly becoming voluminous, there are regrettably few instances in which actual protocols have been recorded. A worker may describe a new technique in great detail, but the result of using it is represented by a graph, (sometimes bearing practically no indication of the magnitudes involved) on which the points through which the Standard curve is drawn are shown as a series of crosses. From this, by measurement and calculation, one can laboriously deduce approximately what the original mean responses and doses may have been; but no idea of the agreement between replicates or of the validity of the results can be obtained, since the actual titrations are not shown and no typical Test Preparation is included. This neglect of the numerical, as opposed to the experimental, details of new analytical work in general is to be deplored. It is as important to be able to check the first as the second—in fact, more so; few will wish to learn about a new and elegant method of obtaining inaccurate results. I strongly urge that no publication of a new analytical technique in this field at any rate should be regarded as complete or accepted for publication unless it includes the protocols of a typical assay.

Examination of the few published dose - response curves from which reasonably accurate estimates of the original data could be made eventually showed that when the logarithms of both the doses *and the responses* were plotted against each other the resulting points were fitted reasonably well by a straight line, at least over a certain range. The enquiry was then extended to a number of assays for both amino-acids and vitamins, performed in four different laboratories, the protocols of which were made available to me by the most willing co-operation of the workers concerned. The linear "log - log" relationship, as it may be called for brevity, was found to hold good almost without exception, though not always over the whole range of doses used. This, of course, is to be expected; the linear relationship found in riboflavine and nicotinic acid assays holds only up to a titration of 8 to 9 ml. of 0·1 *N* sodium hydroxide at most, in terms of response (which is the correct criterion[6]), whereas the doses used in amino-acid assays are usually chosen to give a maximum response of 12 to 13 ml. or even more.

A typical instance of an assay in which the log - log relationship holds is shown in Fig. 1, an assay of threonine by means of *S. fæcalis*, as described by Barton-Wright[4] and performed by him. The curves obtained by plotting dose against response, for both the Standard and the Test Preparations, are transformed into two straight lines when log-dose is plotted

against log-response. The range of linearity is at least from 20 to 80 μg. in terms of dose, or from 3·55 to 9·05 ml. of 0·1 *N* alkali in terms of response.

The log - log relationship appears to fit nearly all the assays on which it has so far been tried. Table I summarises the position. The technique used in these assays is by no means standardised: the test organisms used differ from worker to worker; even where the same organism is used the basal medium may differ. The variations in slope and in range shown in the table are thus not at all surprising.

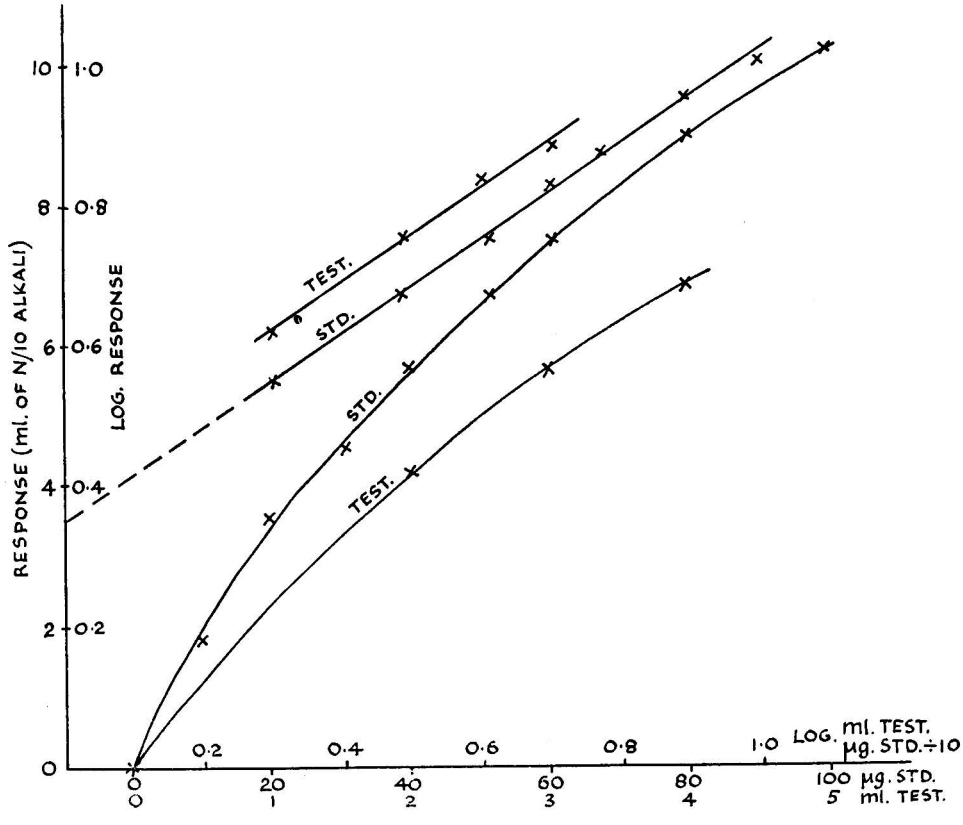

Fig. I. Assay of Threonine with *S. fæcalis*.

Certain entries call for special mention. The assay of glutamic acid is biochemically unusual, since it appears that the substance utilised by the test organism is not glutamic acid but glutamine,[7] and this results in the dose - response curve being initially almost horizontal, restricting the range of linearity, while the next part of the curve is steeper than usual. The technique of this assay is not satisfactory. The assay of proline, as conducted in the Glaxo Laboratories, was different from all the other assays in giving a linear relationship between log-dose and the response itself; and it is interesting that the basal medium used by them for this assay differs from that used by them for all the other amino-acids in the table.

One or two of the assays probably have a greater range of linearity than that shown because the doses were not well chosen to test the point (see below). For example, in the assay of histidine referred to, the lowest dose used was 10 μg. and the corresponding mean response was 6·15 ml. Had doses of 5 μg. and even less been used it is quite probable that the range of linearity would have been extended usefully downwards. This applies also to other assays.

The computation of the mean result and its standard error, and the examination of the validity of the assay, have been fully described elsewhere, notably by Irwin,[8] for all assays in which either the response itself or some function thereof (the response metameter, as Bacharach[9] has called it) is linearly related to the log-dose. But for those who are not familiar with the principles involved, a brief summary may be useful.

(*a*) If the Standard points lie satisfactorily on a straight line between certain limits of response, so should the Test points lie within the same limits. (Any experimental observations outside these limits are best ignored in the subsequent calculations.) Significant curvature in the Test line would render the validity of the assay suspect. Moreover, the Test line should be parallel to the Standard line, and significant lack of parallelism is again evidence of invalidity.

TABLE I

ASSAYS FOUND TO BE MADE LINEAR BY THE "LOG - LOG" TRANSFORMATION

Substance assayed	Reference*	Test organism	Upper limit / Lower limit of response	Slope	Remarks
Amino-acids:					
Arginine ..	B	*Strep. fæcalis*	2·98	0·82	
	G	*Strep. fæcalis*	2·02	0·52	
Cystine ..	B	*Lact. arabinosus*	2·26	0·45	
	G	*Leuc. mesenteroides*	2·02	0·33	
	V	*Lact. arabinosus*	2·32	0·78	
Glutamic acid ..	G	*Leuc. mesenteroides*	1·87	1·16	Linearity doubtful
Histidine ..	G	*Strep. fæcalis*	1·67	0·36	Lower limit probably too high
*Iso*leucine ..	B	*Lact. arabinosus*	3·18	0·65	
	G	*Leuc. mesenteroides*	2·25	0·58	
	V	*Lact. arabinosus*	2·52	0·85	
Leucine	G	*Strep. fæcalis*	3·37	0·69	
	V	*Lact. arabinosus*	2·24	0·76	
Lysine	B	*Leuc. mesenteroides*	4·97	0·70	
	G	*Strep. fæcalis*	2·86	0·58	
	V	*Leuc. mesenteroides*	2·99	0·69	
Methionine ..	B	*Leuc. mesenteroides*	2·90	0·79	
	G	*Leuc. mesenteroides*	2·01	0·42	
	R	*Lact. arabinosus*	3·57	0·74	
Phenylalanine ..	B	*Leuc. mesenteroides*	3·73	0·73	
	G	*Leuc. mesenteroides*	3·07	0·46	
Proline	G	*Leuc. mesenteroides*	Linear, log-dose against *response* 3·3 to 14·05 ml. of 0·1 *N*		
Threonine ..	B	*Strep. fæcalis*	2·55	0·68	
	G	*Strep. fæcalis*	3·13	0·72	
Tryptophan ..	B	*Lact. arabinosus*	7·4	0·76	
	G	*Lact. arabinosus*	6·08	0·84	
	V	*Lact. arabinosus*	2·87	0·67	Lower limit probably too high
Tyrosine ..	G	*Leuc. mesenteroides*	3·20	0·83	
	Gu	*Lact. delbrückii*	2·61	0·72	
Valine	G	*Strep. fæcalis*	1·72	0·60	Linearity doubtful
Vitamins:					
Biotin	D	*Lact. arabinosus*	2·83	0·45	
	Vl	*Lact. arabinosus*	2·74	0·71	
Folic acid ..	J	*Lact. helveticus*	2·13	0·58	
Riboflavine ..	Ro	*Lact. helveticus*	3·58	0·56	

*REFERENCES

B = Dr. E. C. Barton-Wright.
D = The Distillers' Co., Ltd.
G = Glaxo Laboratories, Ltd.
Gu = Gunness *et al.*, *J. Biol. Chem.*, 1946, **163**, 159.
J = Johnson, B. C., *Ibid.*, 1946, **163**, 255.
Ro = Roberts, E. C., and Snell, E. E., *Ibid.*, 1946, **163**, 499.
R = Riesen *et al.*, *Ibid.*, 1946, **165**, 347.
V = Vitamins, Ltd.
Vl = Virol, Ltd.

(*b*) Assuming that the lines are straight and parallel between approximately the same limits of response, the best and quickest way of computing the result is to measure the *horizontal* distance from the Test line to the Standard line. When this is added to the logarithm of the potency of the Standard Preparation, the sum is the logarithm of the potency of the Test Preparation. For example, in Fig. 2, which represents an assay of lysine by Mr. S. A. Price, of Vitamins, Ltd., using *Leuconostoc mesenteroides*, the horizontal distance

along the line "log-response = 0·75" is 0·765 − 0·421 = + 0·344; (note that the Standard figure must be taken first). The Standard Preparation in this assay was pure lysine, and the unit was 10 μg., so that its logarithm is 1·000. Hence 1 unit of the Test extract, which here is 1 ml., contains antilogarithm 1·344 = 22·1 μg. of lysine. Knowing the dilution of the Test extract, one can readily calculate the potency of the original Test substance. In this assay the lines are not quite parallel, and the measurement was taken near the mid-point. A better procedure, which also gives an indication of the validity of the assay, is to make the measurement near the extreme limits of linearity and examine the agreement between the two resulting estimates of potencies. If agreement is good, the mean is taken as the answer. For log-responses of 0·5 and 0·9, the corresponding estimates of the Test extract potency in Fig. 2 are 21·5 and 22·5 μg. per ml., with a mean of 22·0. The extremes are within 3 per cent. of the mean, which is satisfactory.

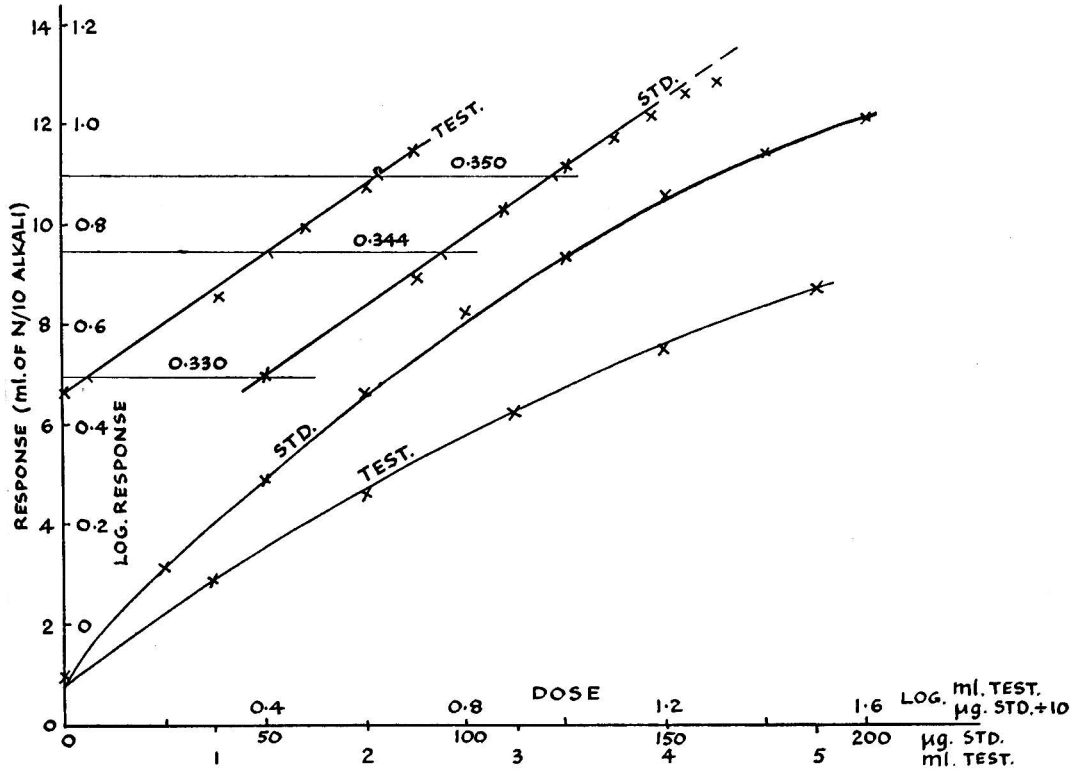

Fig. 2. Assay of Lysine with *L. mesenteroides*.

When the lines are not perfectly parallel the theoretically best estimate of the result is obtained only by a rather lengthy arithmetical process, because the experimental designs at present employed lead to unequal spacing of the dose-levels when plotted on a logarithmic scale and the number of Test doses between the limits of linearity is hardly ever equal to the number of standard doses between the same limits. This means that the slopes of the two lines will usually be determined with unequal precision. Moreover, converting the responses into logarithms usually results in a decrease in variance with increasing dose, which gives more weight to the observations at the higher dose-levels. Consequently, the top half of each line has usually more weight than the bottom half and the weighted mean of the results is not exactly at the mid-point. Mr. D. J. Finney, in correspondence on this subject, gives it as his opinion that "usually the two methods [the graphical and the full statistical] would lead to estimates of potency in very close agreement, but there is a possibility that your method if adopted generally and uncritically might fail to point out invalid assays, and might occasionally give a misleading potency estimate. Further investigation of this point, especially by the detailed study of numerical examples,

is needed as a research project." If an estimate of the confidence limits of the result, or a quantitative test of validity, is needed, then the appropriate calculations, lengthy though they are, will have to be carried out in full in any event. The moral is that the faults of the design should be eliminated as suggested below, which would have the double advantage of simplifying the arithmetical work if the full statistical calculations are carried out and also of reducing risk of error if the quick graphical method is employed. The technique of the statistical method is not new and will not be described here; reference may usefully be made to the paper by Irwin[8] already mentioned.

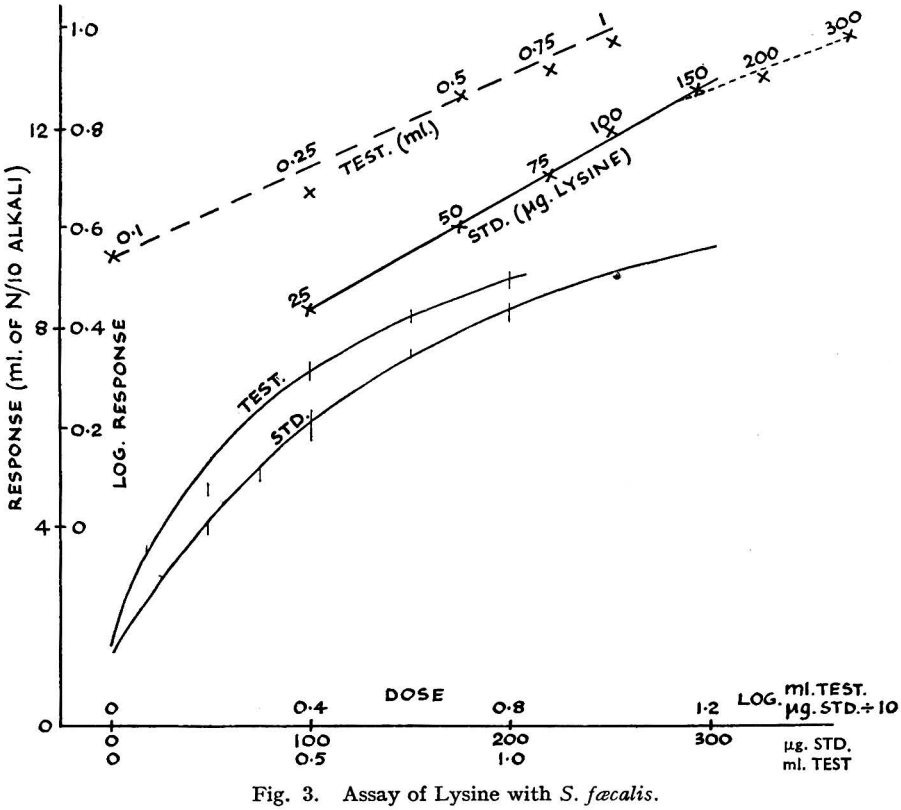

Fig. 3. Assay of Lysine with *S. fæcalis*.

If the "log - log" relationship is found as a matter of experience to hold over a reasonable range, then certain suggestions immediately follow for improving the design and simplifying the computation of the assay. In the first place, the position of the line will be fixed most precisely for a given number of doses, if not they but their logarithms are equally spaced, which means that the doses both of the Standard Preparation and of the Test Preparation should be in geometrical progression. In the example shown in Fig. 2, for instance, the doses used increase uniformly by 25 μg. or 1 ml. as the case may be. This is a natural arrangement, but the result is that the experimental points on the log - log lines are crowded together at the upper end of each line, which is thus better defined than the lower. Had the doses chosen for the Standard Preparation been 25, 35, 50, 70, 100, 140 μg.—a series in which each is $\sqrt{2}$ times the preceding one—the resulting points would have been separated by a constant difference of 0·15 in terms of log-doses. Similarly, a good series of Test Preparation doses would be 0·5, 1, 2 and 4 ml., each being twice the preceding one. It would be even better if the number of doses, as well as the ratio of consecutive doses, were the same for both lines, for then the design is symmetrical and the computations are simple. As usual, the Test doses should be so chosen as to be equivalent as far as possible to the Standard doses in their content of the factors being assayed.

Once it is decided to adopt the "log - log" transformation as a preliminary to evaluating the result, observations should be confined as far as possible to that part of the dose - response

curve which is rendered linear by the transformation. In Fig. 3, for instance (an assay of lysine by means of *S. fæcalis*), the upper two observations on each of the Standard and Test curves are above the linear portion. This leaves observations at only three dose-levels on which to base the Test line, and makes it difficult to fix its position, particularly if (as in this assay) the "fit" is not good. Four or five equally spaced points on each line should be secured if possible; in this example it would have been practicable to use Standard doses of 10, 20, 40, 80, and 160 μg., with Test doses of 0·1, 0·2, 0·4, 0·8, and 1·6 ml. Probably the lowest Standard dose and the highest Test dose would have been found to be "off the line"; that would have left a symmetrical design with 4 equidistant points on each line. The resulting computations would then have been simple. This is the kind of design to aim at, at any rate; with any assay performed regularly according to a standardised technique, experience should soon show how to secure it. The *extreme* limits of linearity and the slope will of course vary, not only between laboratories, but even between assays by the same worker; yet the slopes of all the assays in Table I are very much larger than the standard error (usually of the order of 0·01 to 0·03 in these assays), which means that in every instance the fiducial limits of the result should be sufficiently close for all practical purposes if the assay is valid at all, while safe working limits of dosage within which every assay will be linear can be determined by experience for each amino-acid or other nutrient factor separately.

It has been stated above that the "log - log" transformation has the effect in most instances of producing an error variance which decreases with increasing dose. This may be deplorable in theory; in practice, owing to the good agreement between replicates and the excellent approximation to linearity which appears usually to obtain in these assays, the effect on either the accuracy or the precision of the result is unlikely to be large. This point, however, warrants further examination.

While the ratio of the slope to its standard error is the criterion of the inherent precision of an assay technique, the sensitivity with which invalidity will be detected depends on the range of linearity in terms of log-response, which corresponds to the ratio of the upper to the lower limit of linearity in terms of the response itself. The fourth column of Table I shows that there is considerable variation in this respect between assays, but, as previously stated, further work would probably show that the range of linearity can often be extended.

One or two points remain to be made. First, the "log - log" transformation, which is not at all original, is purely an empirical device for expediting the extraction of information from an assay; it is not suggested that there is any profound biochemical significance in the fact that many assays are "linearised" by its use, or that an assay which does not conform to this generalisation is any the worse for it. Secondly, the suggestions made in this paper for improving the design of "log - log" assays are put forward only in the hope that they may prove helpful to those workers who use such assays primarily to obtain quantitative information about the chemical analysis of foods and the like. They are not applicable to the research worker who is investigating the biochemical processes involved, and whose needs are quite different, as Finney[10] has pointed out. Finally, nothing in what I have said must be taken to imply any criticism of the assay protocols on which this paper is based; they are in the main as well constructed as was possible in the absence of any information about a "linearising" transformation or the range over which such a transformation holds.

I am greatly indebted to Dr. E. C. Barton-Wright, to Mr. S. A. Price of the Research Laboratories, Vitamins Ltd., to the Research Division of Glaxo Laboratories Ltd., and to Dr. E. R. Dawson of The Distillers Company Ltd., for their kindness in allowing me to see and use their experimental data, as well as to Mr. D. J. Finney for advice on statistical theory.

Summary

In microbiological assays of many specific nutrients the relationship between dose and response is not linear. It is now found that when the logarithm of the dose is plotted against the logarithm of the response the resulting points are usually well fitted by a straight line over a reasonable range. This makes it possible to compute the best estimate of the result and its standard error, and to test quantitatively the validity of the assay, by methods which accord with accepted statistical principles. The assay can be made more efficient and the calculations simplified by modifying the experimental design. The doses of both the Standard and Test Preparations should be in geometrical, not arithmetical, progression, and the assay should be as far as possible symmetrical in the number and spacing of the doses,

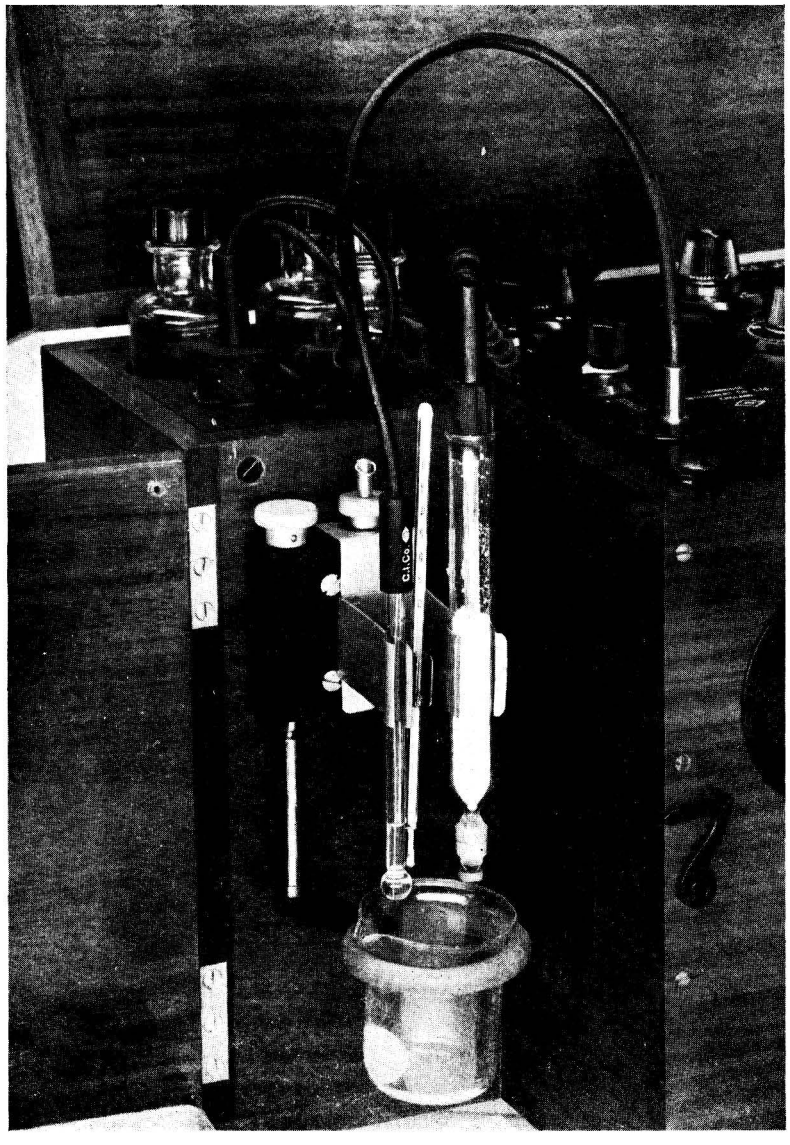

Fig. 1. *p*H Meter with screened lead from glass electrode to earthed instrument panel.

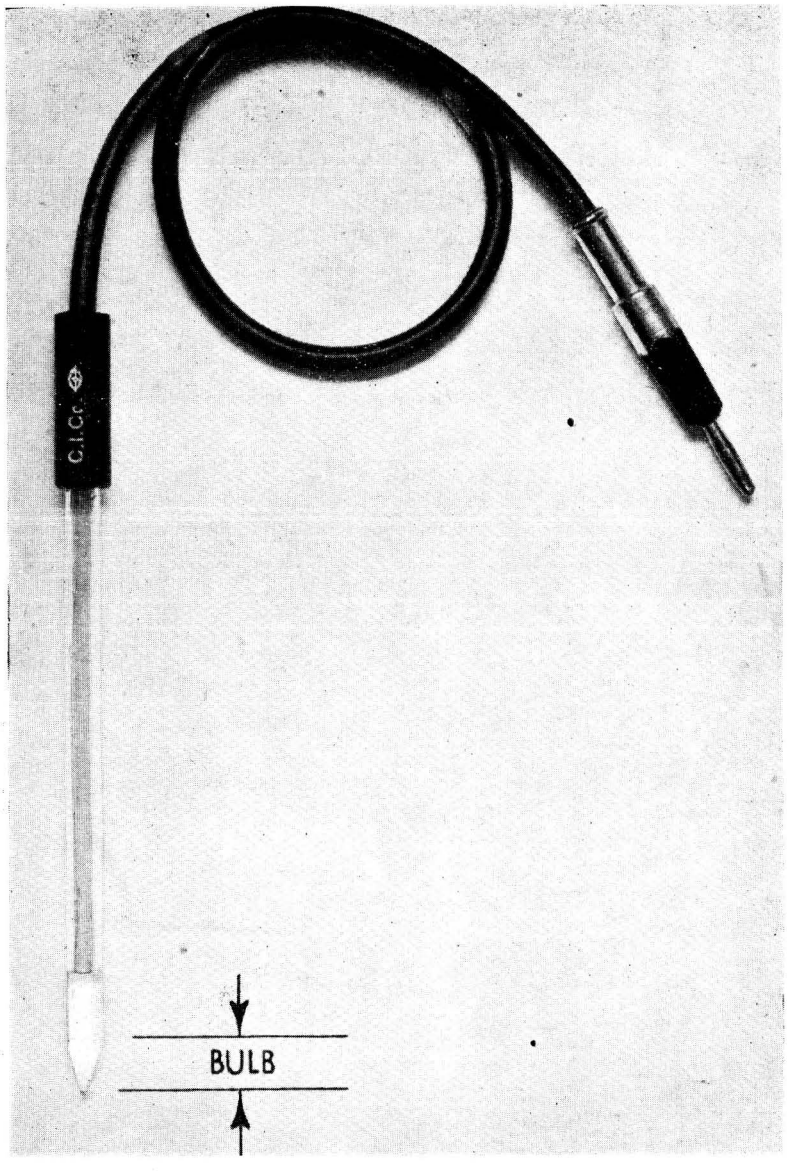

Fig. 2. Spear Type Glass Electrode. Note long insulation (black) between screen and tip of plug.

which should be confined to that part of the dose - response curve which the "log - log" transformation renders linear. Several questions that arise from these considerations need further investigation.

References

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2. Snell, E. E., and Wright, L. D., *J. Biol. Chem.*, 1941, **139**, 675.
3. Report on the Microbiological Assay of Riboflavine and Nicotinic Acid, ANALYST, 1946, **71**, 397.
4. Barton-Wright, E. C., *Ibid.*, 1946, **71**, 267.
5. Price, S. A., *Nature*, 1945, **156**, 171.
6. Wood, E. C., ANALYST, 1946, **71**, 1.
7. Hac, L. R., Snell, E. E., and Williams, R. J., *J. Biol. Chem.*, 1945, **159**, 273.
8. Irwin, J. O., *J. Hygiene*, 1943, **43**, 121.
9. Bacharach, A. L., Coates, M. E., and Middleton, T. R., *Biochem. J.*, 1942, **36**, 407.
10. Finney, D. J., ANALYST, 1946, **71**, 14.

VIROL LTD.
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Discussion

Mr. S. A. PRICE said that the use of closely-spaced doses in geometrical progression was quite practicable, and was in fact normal in serological testing, when doses each of which was 110 per cent. of the preceding one were commonly used. He asked whether the log - log transformation had been found applicable to a large proportion of the assays examined. If assays were designed on the lines suggested, then those occasional assays that did not conform to the log - log relationship would be difficult to evaluate by the direct-reading method.

Dr. E. R. DAWSON reported that he had found the log - log relationship to hold over a wide dose-range for a long series of biotin and pantothenic acid assays using *L. arabinosus*. He was now trying in his laboratories a four-point assay design with a dose-ratio of 4 for both standard and test substance. The log - log relationship could not be expected to be linear at very low dose-levels in assays which do not give a blank of zero. Had Dr. Wood considered this point?

Mr. E. C. FIELLER pointed out that Dr. Wood's suggestion that the linear range might be usefully extended downwards in certain instances by using smaller doses might lead to trouble if carried too far, since the variance of the response after logarithmic transformation must tend to increase with decreasing response, and would become excessively high below a certain value of response.

Dr. WOOD, replying to Mr. Price, said that Dr. Dawson's experience indicated that the log - log relationship, if it held at all for a given type of assay, was consistently applicable in a large series. Moreover, if an occasional assay were exceptional, the direct-reading method could still be used provided that there were three or more doses of each preparation. It was true, as Dr. Dawson had said, that the log - log transformation could not be expected to "linearise" an assay down to very low dose-levels, and indeed it would be dangerous to go too far downwards for the reason advanced by Mr. Fieller. Each worker should find out for himself, by trial and error, the maximum safe range of doses that could be used in a particular assay technique.

Electrometric Analysis

(The following three papers were read at the Joint Meeting of the Physical Methods Group with the Cardiff and District Section of the Royal Institute of Chemistry and the South Wales Section of the Society of Chemical Industry, at Cardiff, on Friday, October 11th, 1946.)

Recent Developments in Apparatus for *p*H Measurements and Electro-titrations

BY A. D. ELMSLY LAUCHLAN

THE use of the thermionic valve in a *p*H measuring device has enabled manufacturers to supply an instrument so robust and simple to use that even unskilled and semi-skilled workers are now able to make precision measurements.

Ability to use a well designed *p*H meter, however, does not always go with the careful technique necessary for proper use of chemical apparatus, and much trouble and annoyance have been the lot of many when the glass electrode has been broken owing to a moment's carelessness. It has been the aim of the instrument maker to produce electrodes as robust as the associated instrument, and to this end thicker and thicker glass electrodes have been produced, so that now if the modern glass electrode is knocked on the bench the stem is more likely to be broken than the bulb.

It should be appreciated that the difficulties of making glass electrodes stronger have been not in the actual blowing of the bulb but in arranging conditions so that the very minute amount of energy available can be applied to the measuring circuit without appreciable loss.

When it is remembered that the resistance of a glass electrode is of the order of 150 to 200 megohms, it will be understood that the leakage permissible must be extremely small in order to obtain an accuracy of 0·1 per cent.; a leakage resistance of 1000 megohms will lower the efficiency of the system by about 8–9 per cent.

Improvement in insulation alone will not make the measuring instrument read correctly if the valve is not suitably chosen or arranged to have the correct condition in which the grid takes a negligible current, *i.e.*, 10^{-12} amperes at the most. Most modern instruments are no longer fitted with the electrometer valve, which did not lend itself to sub-panel mounting and, moreover, was somewhat sensitive to shock. The great advantage of the electrometer valve was its very high grid resistance, but it is now possible to use some of the more conventional types of valves and so adjust their working conditions that they act as electrometers or very nearly so. The use of these smaller valves has given greater stability to mechanical shock, enabling a much steadier electrical zero to be maintained, and has allowed the manufacturer to produce a neater instrument.

When the grid of a valve is connected to a source of potential having a high internal resistance, *e.g.*, a glass electrode, the circuit becomes very sensitive to stray electrostatic charges such as arise when the connecting cable of the electrode is touched or moved, and this gives rise to much annoyance by causing the galvanometer needle to wander.

This trouble can be overcome only by shielding the circuit and connecting the shield to earth, but this shielding must extend from around the valve right up to the electrode and much ingenuity has been exercised in devising a simple connection for the glass electrode, suitably insulated and shielded so that the user has the benefit of high insulation and correct shielding (Figs. 1 and 2). This problem becomes even more acute when long lengths of cable, often up to 200 feet, have to be used. The problem occurs more with industrial recording instruments than with laboratory apparatus, but that it has been successfully overcome indicates that the principles employed are right.

These apparently small changes have in reality done much to permit the use of stronger electrodes, which are, at the same time, less disturbed by stray electrostatic charges.

There are now appearing in England direct-reading *p*H meters or rather indicators, which show at a glance the actual *p*H value or any change occurring in it without any further manipulation of the instrument controls. These instruments undoubtedly have a great advantage over the type that requires balancing by hand, but it must be remembered that their accuracy will, in general, not be as good as that of a null-method instrument, since the deflection of the pointer is determined by the characteristic of the valve, which may change. A further point is that the limited scale length, even with a double scale of *p*H 0 to 7 and 7 to 14, one cannot read accurately to 0·01 *p*H, which is quite often required.

The null-point instrument and the direct-reading indicator really fill two separate requirements, the first giving high accuracy where speed of operation is not quite so important, the second giving a somewhat lower accuracy of $\pm$ 0·05 *p*H, which for very many problems is quite sufficient. The popularity of the direct reading indicator in the U.S.A. is an indication of its usefulness.

The so-called "magic eye" indicator has not so far replaced the galvanometer in English *p*H meters, as has already happened in some instances in America, probably because the range of valves suitable for convenient incorporation in the instrument is not yet readily available here.

From an examination of these indicators it does not seem easy to judge the balance point to an accuracy of 0·01 *p*H, possibly because there is no real fiducial point from which to measure the change; also the general sensitivity seems to be lower than that of a galvanometer. The cost of the electronic indicator and its associated equipment is not likely to prove less than that of a good galvanometer, and while they may be less sensitive to mechanical damage a well made galvanometer can also stand up to rough usage.

It is, moreover, interesting to see that many American manufacturers are still using the galvanometer as the sensitive detector, so it may be a matter of doubt as to whether the electronic form of detector can strictly come under the heading of improvements.

Turning now to the glass electrode itself it has been found that the best results are obtained if the glass is made from very pure materials so that impurities, chiefly alumina,

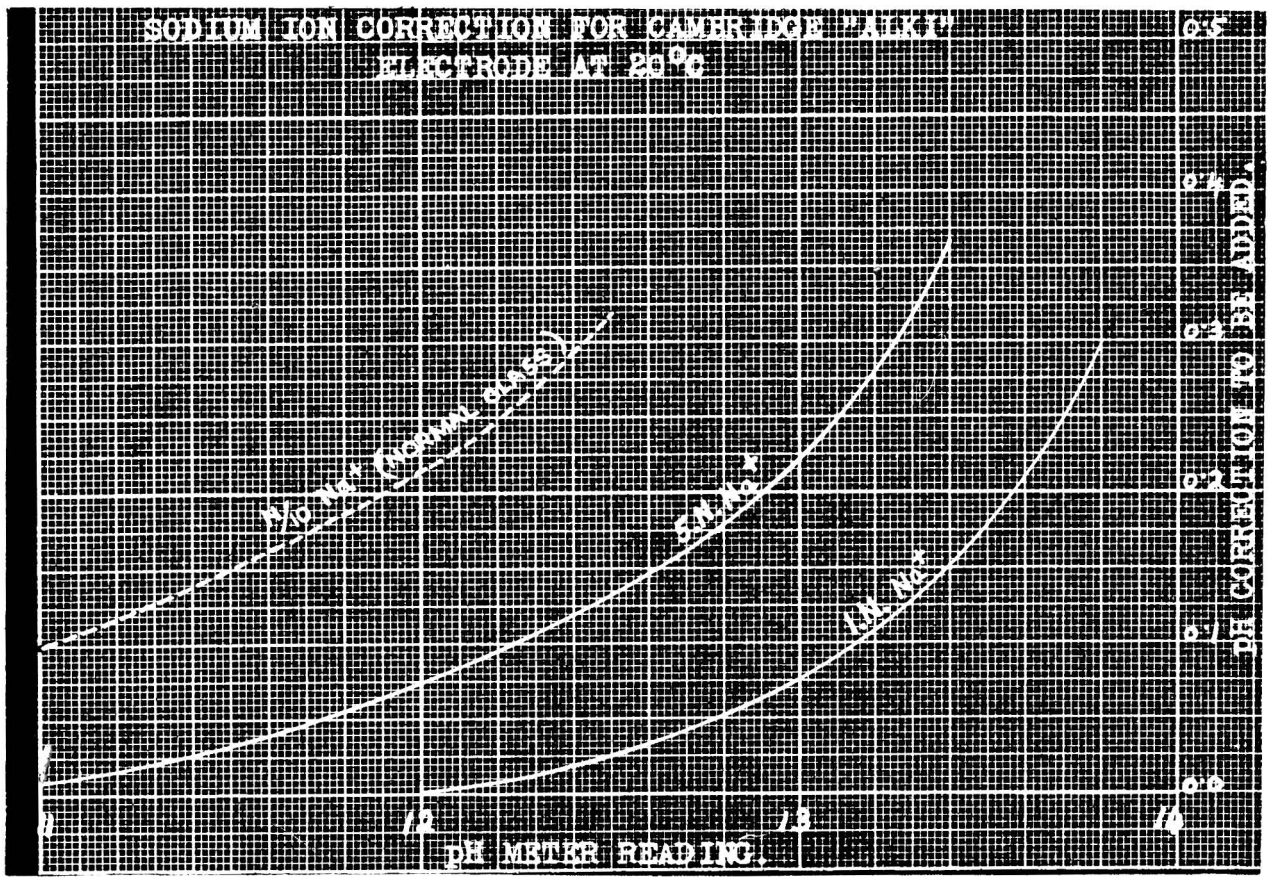

FIG. 3

Curve showing corrections for high *p*H glass electrode. Dotted curve shows error of normal glass electrode.

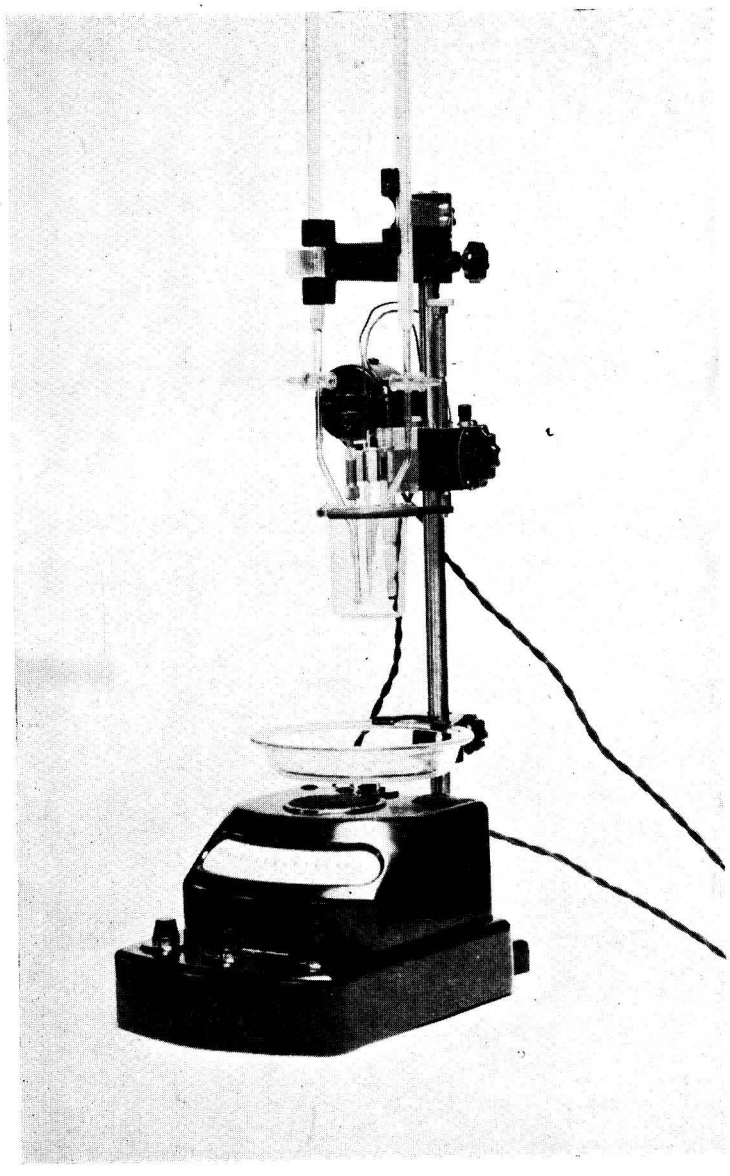

Fig. 4. Potentiometric Titration Apparatus fitted with galvanometer.

are kept as low in amount as possible, generally 0·25 per cent. The production of pure glass enables an electrode to be made which will give theoretical results over a wide range of *p*H. The use of the pure glass enables us to make very small electrodes, which are yet sufficiently conducting to give theoretical results over the same range as the normal electrode. These small bulbs, which may be only 2·5 mm. in diameter, are exceedingly useful for examining small quantities of material or for carrying out electro-titrations on a few drops of liquid, such as might be used in a Conway vessel. The small electrodes also find considerable use in medical and dental work, such as the examination of saliva in the pockets formed between the cheek and the gums.[1] When fitted with a correctly shielded lead these electrodes give very steady potentials on a *p*H meter.

Probably the most outstanding improvement in glass electrode performance is the production of a glass which is less sensitive to sodium ions and enables accurate measurements to be made up to *p*H 14 and in solutions more concentrated than 1 Normal. The improvement in performance can be judged from the fact that the normal glass electrode has a sodium error of about 0·6 *p*H at *p*H 12 whereas the new glass reduces this error to zero even on a 1 Normal solution of sodium ions (Fig. 3). While it is necessary to know the sodium ion concentration in order to apply the appropriate correction to obtain the best results, the error introduced by an uncertainty of the ion concentration is not nearly so serious. The general accuracy of this new glass electrode is about 0·02 *p*H. For those who are not acquainted with this new electrode it may not be out of place to point out that, while the electrode can give accurate results in the acid range below about *p*H 9, it offers no advantage at all over the normal electrode, and exposure to an acid medium for any length of time ages the glass so that its response in the higher range of *p*H values is spoiled. The new glass can be made into bulbs of the usual shape and size and, apart from any special identification mark put on by the makers, cannot be distinguished from the normal type.

The reference electrode to be used with glass electrodes has undergone but little change except that for some purposes, such as medical, the usual ground sleeve type of junction has been replaced by a sintered plug, which can, if need be, take the form of a fine pointed tube, so as to occupy only a small part of the space available when micro tests are being made, or where it is necessary to introduce the cell connection into cavities in the body, *e.g.*, the mouth.

The general trend of electrode structure is to have the electrodes stronger and smaller, and in the future it may well be possible to reduce the present sizes even more.

In the field of recording and control of *p*H values, the general principles which have produced improvements in manually operated instruments also hold, and the changes that have enabled closer control to be maintained in batch and flow processes are applicable to all types of controllers, but these are rather outside the present subject.

In spite of the fact that the literature on potentiometric titrations extends back over a considerable number of years, there does not seem to have been any great application of the methods until the last war. Possibly the need for a large number of routine analyses to be carried out by semi-skilled workers called for a simpler apparatus than had been available before. The earlier forms of electro-titration apparatus, developed mainly by Dr. Sand, were rather akin to some of the earlier *p*H meters and did not lend themselves to easy operation or understanding by the semi-trained. The use of the hydrogen electrode, with all its attendant troubles, no doubt accounted for their lack of popularity.

The rapid increase in the pace of war production made the demand for a simpler electro-titration apparatus more urgent. The experience gained in the development of *p*H meters was now directed to improving an old but otherwise useful apparatus, so that we now have something which bears but little resemblance to the collection of parts, which formed the prototype apparatus.

The modern sensitive galvanometer and the "magic eye" are now competing for the place of detector, and here at any rate the "magic eye" seems to have an advantage since it can be mounted on the burette stand. The slightly lower sensitivity of the "magic eye" detector is not so important here as, unless the conditions of the reaction going on in the beaker are not well chosen, there should be a reasonably large change of potential at the end-point. It may, perhaps, be permitted to remind the user that no matter how good the instrument may be, the best results cannot be obtained unless the conditions of the chemical reaction are properly arranged, for the indicator electrode can only pass on to the detector the results of the change that it experiences in the reaction.

Here again English and American practice seems to offer fairly equally the two forms of detector, so that it would appear that opinion as to the better type is still undecided.

The electro-titration apparatus (Fig. 4) now consists of a stand carrying the burettes and possibly an indicator of the end-point and a small box in which are placed the potentiometer and any amplifier for operating the detector. The potentiometer may be calibrated in millivolts or left uncalibrated; it is not very important which system is used, as in general it is only necessary to balance out the initial potential developed by the electrodes and then note by means of the movement of the detector the change in this potential at the end-point.

The instruments are battery- or mains-operated, depending on the use of a galvanometer or "magic eye" detector, and there is little to choose between them as a matter of convenience.

While the uses to which the electro-titration apparatus may be applied hardly come under the heading of "recent developments," it may not be out of place to mention some of the newer applications.

The beautiful method devised by Foulk and Bawden[2] in the U.S.A. and known as the "dead-stop end-point," uses two noble metal electrodes which are polarised by the passage of a current until an excess of one reagent depolarises them and causes a large increase in the current through the detector; alternatively the current can be reduced almost to zero by addition of a reagent that reacts with and removes the depolariser.

The titration of thiosulphate or sodium arsenite with iodine produces the first condition and the inverse operation provides the second. The system has, therefore, a very wide scope of application and has been used for the determination of oxygen in turbine condensate[3] and for the estimation of moisture by the Karl Fischer method,[4] in which iodine in dry pyridine, saturated with sulphur dioxide, is caused to react with the water in the test material.

It is a matter of regret that so far no chemical manufacturer has put on the market the necessary reagents, but from enquiries made this deficiency is shortly to be remedied. Admittedly it is a somewhat revolutionary method of determining moisture but the oven drying method is not above reproach.

An examination of current literature will provide a far more suitable source of information on electrometric titration than can be compiled in a short paper of this description, since it ranges from the determination of vitamins to steel analysis, but it may not be out of place to point out that the elegant method of Foulk and Bawden can often be applied more satisfactorily than that in which a change of potential takes place, *e.g.*, reactions involving the use of potassium permanganate.

Conductometric titrations do not seem even yet to have become so widely used as the potentiometric method and its modifications, possibly because more trouble is caused by the comparatively large temperature coefficient of resistance of a solution, which requires much greater care to be taken to ensure constancy of temperature during the experiment.

There are available now very satisfactory conductance bridges operating at about 1000 cycles per second, fitted with a telephone and a galvanometer or a "magic eye" as detector of balance, so there does not seem to be any obvious reason why this analytical method has not progressed like the potentiometric.

It is perhaps not too much to expect that the future will bring, and at no very distant date, further improvements in the instruments themselves and also in the glass electrodes, the working of which we are as yet only beginning to understand. The recent advances have opened up a field of thought which may well provide some very interesting results.

Thanks are due to the Directors of the Cambridge Instrument Co., Ltd., for permission to make use of data obtained in their work and for the loan of instruments.

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Some Applications of Electrometric Methods in Analysis

By R. J. CARTER

This paper endeavours to review a few of the more useful electrometric methods available for use in quantitative analysis and also to observe some new trends in analytical research prompted by those methods. The scope of the paper is necessarily restricted and many examples, including the whole group of conductometric methods, are consequently omitted. Reference will be confined to potentiometric titrations, divided into sub-groups of acid - alkali, precipitation and oxidation - reduction types, concluding with some considerable reference to the mechanism and application of the Karl Fischer reagent electrometric method for the determination of small amounts of water.

Probably the widest review with bibliography of potentiometric titrations is that given by Furman,[1] who gives references to published work over the last twenty years, and has himself made many valuable contributions. For detailed methods of many types, the analyst is recommended to refer to that review.

Acid - alkali titrations

The relative ultimate accuracy of indicator and potentiometric methods largely depends upon the appearance of inflection in the neutralisation curve. In general, the latter is governed by the magnitude of the product K.C relative to the ionisation constant of the solvent, where K is the ionisation constant of the weak acid or base and C the concentration.[2] In aqueous solutions no inflection appears unless K.C is greater than 27 K_w,* and for practical purposes K.C should be greater than 10^{-10}. Where the inflection is not sharp it may still be possible to estimate the end-point with fair precision, as the point where the second differential changes sign; if the reagent has been added in equal increments this may be calculated from differences between successive titration values; alternatively it may be found by examination of the graphs of e.m.f. against volume of reagent.

Apart from the obvious application to titrations of coloured solutions, the use of the potentiometric method is of value where the indicator end-point is evanescent, such as with weakly dissociated acids or bases, a practical example being heavily bodied vegetable oils. The reaction towards the end of the titration may be slow, requiring some time for a steady e.m.f. reading at each addition, but the graphical calculation of the equivalence point will be accurate and will give a result truer than that obtained with an indicator.

The titration of materials soluble only in non-aqueous solvents may be carried out by rendering the solutions conductive, *e.g.*, by addition of lithium chloride, or by use of selected solvents. Titrations in non-aqueous media in the latter category have been described by Lykken, Porter, Ruliffson and Tuemmler[3]; one of the criteria required of the selected solvent or solvent blend is that it should have properties such that dissolved acidic materials, with dissociation constants greater than 10^{-7} in water, will ionise sufficiently to permit neutralisation by an equivalent quantity of alcoholic strong base solution. It should be sufficiently conductive to allow only momentary accumulation of electrostatic charges when a low resistance reference electrode is immersed in it. Lykken and his co-workers titrate in a solvent blend of equal parts of benzene and *iso*propyl alcohol containing 1 per cent. of water and use a glass - calomel electrode system. (To avoid using the *p*H unit when referring to non-aqueous solutions, the term cG unit was selected and is given in volts.[4] It was found that most strong acids in the non-aqueous medium gave an inflection near a cG value of 0·236 volts, equivalent to a *p*H of 4·0, and weak acids one at 0·650 volts, equivalent to a *p*H of 11·0. Where definite breaks or inflections are not apparent the titrations to cG 0·236 and 0·650 volts were taken as equivalent to strong and total acids respectively.)

The use of a **titration** curve with more than one inflection to detect different acids and bases present together is well known. It is possible to determine hydrochloric acid in presence of either formic or acetic acid, and these in turn are distinguishable from weaker acidic compounds, such as thiophenol.

Combined acids may be determined by saponification treatment; the differences between titrations for sample and blank to reach a cG of 0·650 volts is a measure of the total free and combined acidic constituents, *i.e.*, the saponification number. The corresponding differences

* K_w = dissociation constant of water.

to reach the lower cG value of 0·236 volts is a measure of the free and combined strong acid constituents only.

A method has been devised whereby saponification numbers of fats and oils can be determined and the need for a blank titration is eliminated.[5] The potentiometric titration curve obtained after saponifying the oil and titrating with acid shows two breaks, the acid added between the two points of inflection being used for the reaction

$$RCOO' + K^{\cdot} + H^{\cdot} + Cl' \longrightarrow RCOOH + K^{\cdot} + Cl'.$$

This is equivalent to the saponification number of the oil, so that a blank titration is not required. It may be that the slope of the graph at the second break is not steep enough to determine accurately. The slope is proportional to $(K.L.V)^{-\frac{1}{2}}$ where K is the ionisation constant of the fatty acid, L is the number of millimoles of fatty acid in solution at the equivalence point and V is the total volume of solution. An increase in slope therefore can be brought about by decreasing L, namely by adding benzene to extract fatty acid into the benzene phase. Inflection points are located by calculating second differentials in the usual way.

The use of non-aqueous solvents to differentiate further the ionisation characteristics of two or more solutes represents a new method of approach in analytical research. By its means it becomes possible to obtain a differential titration which may be unsatisfactory or impossible in aqueous medium. Various workers have investigated the use of acetone - water mixtures, alcohols, benzene and Cellosolves. Lykken and others[3] showed that in the selected blend of *iso*propyl alcohol and benzene the relative acid or base strengths of the members of a series of acids or bases are in the same order as in water, and also showed graphically that there is a relationship between the relative strengths deduced from titrations and the pK_a* values in water.

It is also possible to show by varying the media to different degrees of aqueous content or water-like properties, that a weak acid shows a higher degree of ionisation in water than in non-aqueous media. Strong acids do not follow a strictly regular trend and appear to show a maximum degree of ionisation in solvents that are intermediate in water-like properties. Practically it means that a non-aqueous solvent medium may be chosen in which it will be easiest to distinguish between strong acids whose pK_a (H_2O) values are in a close range.

Precipitation and Oxidation - Reduction Type Titrations

It is not intended to list the applications of these types of titrations—the theory and use of them are too well known. Some contributions by different workers in recent years are of considerable interest, however, and their value may be the more apparent when the findings are applied to other problems.

The use of electrolyte bridges in potentiometric titrations where a bimetallic electrode system cannot be employed often has the disadvantage of the risk of contaminating the test solution. Heintze[6] in 1934 suggested that the glass electrode might be used as a reference electrode as opposed to its usual function as an indicator electrode. It has been established that the glass electrode behaves as a satisfactory reference in potentiometric titrations where the hydrogen ion concentration remains practically constant during the titration and is not a function of the titrant, *i.e.*, where the solution contains excess of acid or base or an effective buffer. Lykken and Tuemmler[7] have published results showing typical potential - volume curves for argentimetric and oxidation - reduction titrations. The titrations selected include instances in which two different titrate ions are present and the graphs show very satisfactory two-break curves. Using 0·1 *N* alcoholic silver nitrate and a titration medium of 0·1 *N* alcoholic sodium acetate, it is possible to determine hydrogen sulphide and thiophenol quantitatively in presence of each other. This procedure may be compared with the Institute of Petroleum method investigated by Davies and Armstrong for estimating mercaptans in petroleum products.[8] In the latter instance, nydrogen sulphide is first removed by shaking with cadmium sulphate and then the titration is carried out by means of a silver - alcoholic sodium acetate - mercury electrode system. Elementary sulphur is determined at the same time, giving an early break in the titration curve due to the greater insolubility of silver sulphide as compared with silver mercaptide. Temele and Ryland,[9] who first devised this method, suggested the possibility of determining both hydrogen sulphide

* pK_a = acid strength expressed as the negative exponent of the logarithm of the acidity constant K_a.

and mercaptan when present together, but favoured the removal of any elementary sulphur by prior shaking with mercury, in view of the possible reaction between the sulphur and the mercaptan in the alkaline conditions of the titration.

Other argentimetric titrations, using the glass reference electrode, include the co-determination of iodide and chloride ions and also thiocyanate and chloride. Oxidation - reduction examples, include titration of stannous and ferrous ions, singly or together, with ceric sulphate, and titration of permanganate, vanadate and bichromate with ferrous sulphate. The advantages of using an easily prepared and non-contaminating reference electrode in all these methods are apparent.

A useful potentiometric method is that using the "bottled end-point" described by Callan and Horrobin,[10] in which the reference electrode potential should be the same as the indicator electrode potential at the end-point. An interesting application of the titration of chloride ion using the "bottled end-point" is the method described by Haslam and Sweeney[11] for the determination of aniline in presence of secondary and tertiary amines. The reaction between aniline and picryl chloride is utilised and sodium bicarbonate is present to neutralise and fix the hydrochloric acid liberated in the reaction.

A noteworthy recent contribution of oxidation - reduction type is the determination of nitroguanidine[12] by decomposition with concentrated sulphuric acid and titration of the nitrate ion with ferrous ammonium sulphate by means of a platinum - tungsten electrode system. The method is of interest because of its possible application to the determination of nitro-urea.

Polarisation end-points provide a type of titration which is finding increasing use. A characteristic feature is the rapidity with which the system reaches an equilibrium at each addition of titrant near to the end-point as opposed to the pause usually necessary with orthodox potentiometric end-points. Foulk and Bawden[13] described the application of the "dead-stop end-point" to iodine - thiosulphate titrations. They used a small e.m.f. of the order of 15 millivolts between two platinum electrodes in the titrate solution, this e.m.f. being ultimately balanced by the back e.m.f. of polarisation of one of the electrodes. They deduced that a dead-stop end-point would occur in all reactions which coincided with the sharp transition from the polarisation of at least one electrode to the complete depolarisation of both of them or *vice versa*.

The application of this end-point to the determination of dissolved oxygen in water and its advantage over the starch indicator end-point have been described by Evans and Simmons[14] and Sillars and Silver.[15] Another application is the titration of ascorbic acid with 2:6-dichlorophenolindophenol in coloured solutions.[16] In this titration, excess of dye depolarises the cathode and the dead-stop end-point is observed as a permanent current surge. The response is instantaneous and has that advantage over the potentiometric titration with a mercury-coated platinum and calomel electrode system.

Electrometric titration with Karl Fischer reagent

The importance of the Karl Fischer reagent[17] as a quantitative reagent for the determination of small amounts of water is evident from the volume of published work on this subject. It would appear that the applications are almost without limit and, in fact, foundation for further work in the quantitative analytical organic field has been truly established by the work of Smith, Bryant and Mitchell.[18] They have utilised the production or use of water in a number of organic reactions as a means of estimating organic radicals. Alcoholic hydroxyl groups may be acetylated and methyl esters formed from aliphatic acids, both with the production of a stoichiometric amount of water. Similarly carbonyl compounds can be determined from the water produced by their reaction with hydroxylamine hydrochloride. Acid anhydrides are hydrolysed with a slight excess of water, with sodium iodide as a catalyst, and the unused water determined. Other examples of the application of Karl Fischer reagent are the determination of water of hydration of salts, analysis of mixtures of primary, secondary and tertiary amines, and the determination of nitriles and amino alcohols.

Karl Fischer had suggested the use of an electrometric end-point, where the visual titration was not possible, and later Almy, Griffin and Wilcox[19] described the potentiometric back titration of excess of Fischer reagent with a standard water solution, using a platinum - tungsten electrode pair. Disadvantages were the usual wait until equilibrium was reached after each addition and the need for resensitising the tungsten electrode. The application of the "dead-stop end-point" of Foulk and Bawden was suggested by Wernimont and

Hopkinson,[20] whose method involved less manipulative difficulties. Further refinements were introduced by McKinney and Hall,[21] who used a "magic eye" indicator and a titrimeter circuit similar to that of Serfass. In both of these "dead-stop end-point" methods a potential of the order of 15 millivolts is impressed on the two platinum electrodes. Polarisation of the cathode occurs when the iodine is totally consumed at the end-point, the resulting back e.m.f. counterbalancing the applied e.m.f. to give no observable current. It was stated that the direct titration of water-containing solutions with Fischer reagent gave premature and fading end-points. Later workers[22,23] showed that a direct titration could be carried out satisfactorily. A much higher e.m.f. of the order of 1 to 2 volts can be applied and a sensitive galvanometer used by shunting with a small resistance.

It is the accepted theory that in the direct titration the cathode is depolarised by excess of iodine at the end-point. The writer has made measurements of change of resistance and current and finds that support for this theory can be obtained by calculating both the apparent electrode potential and the applied potential across the electrodes throughout the titration. The graphical representation of the change of current and resistance of the electrode system as the titration proceeds is shown in Fig. 1. The resistance was measured at each addition,

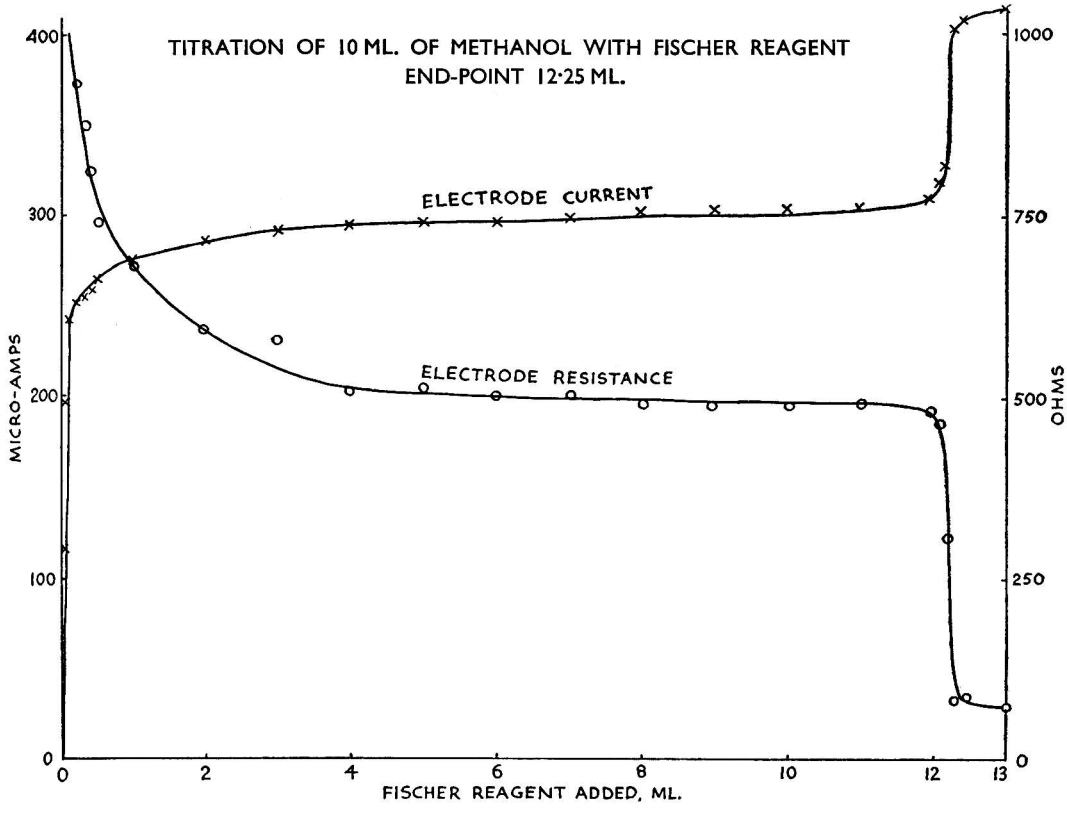

FIG. 1

using an ohm meter. The circuit was as described by Carter and Williamson,[22] and consists of a 2-volt cell, the electrode pair, a 5000-ohm resistance and the galvanometer in series, the latter having a 10-ohm shunt resistance. The galvanometer used in this experiment had a resistance of 808 ohms and a sensitivity of 60 mm. per micro-amp. It will be seen from the circuit that, if R_e is the resistance of the electrodes immersed in the titrated solution, then at any point in the titration the applied potential drop across the electrodes may be calculated from the resistance, by using the expression

$$\text{Applied potential} = \frac{R_e}{R_e + 5010} \times 2 \text{ volts.}$$

The apparent potential may be deduced from the current, by using the expression

$$\text{Apparent potential} = I_e \times R_e \times 10^{-6} \text{ volts},$$

where I_e is the current flowing across the electrodes, in micro-amps., *viz.*, galvo current × (galvo + shunt resistance) ÷ shunt resistance. It was found that at the commencement of the titration the e.m.f. applied was approx. 0·3 volt greater than the apparent e.m.f., and that this difference decreased rapidly to a value of about 30 millivolts, which was maintained during the greater part of the titration. We may regard this difference as a measure of the back e.m.f. or polarisation e.m.f. At the end-point of the titration the value suddenly decreases to zero, corresponding to the depolarisation of the cathode. The values derived are shown graphically in Fig. 2.

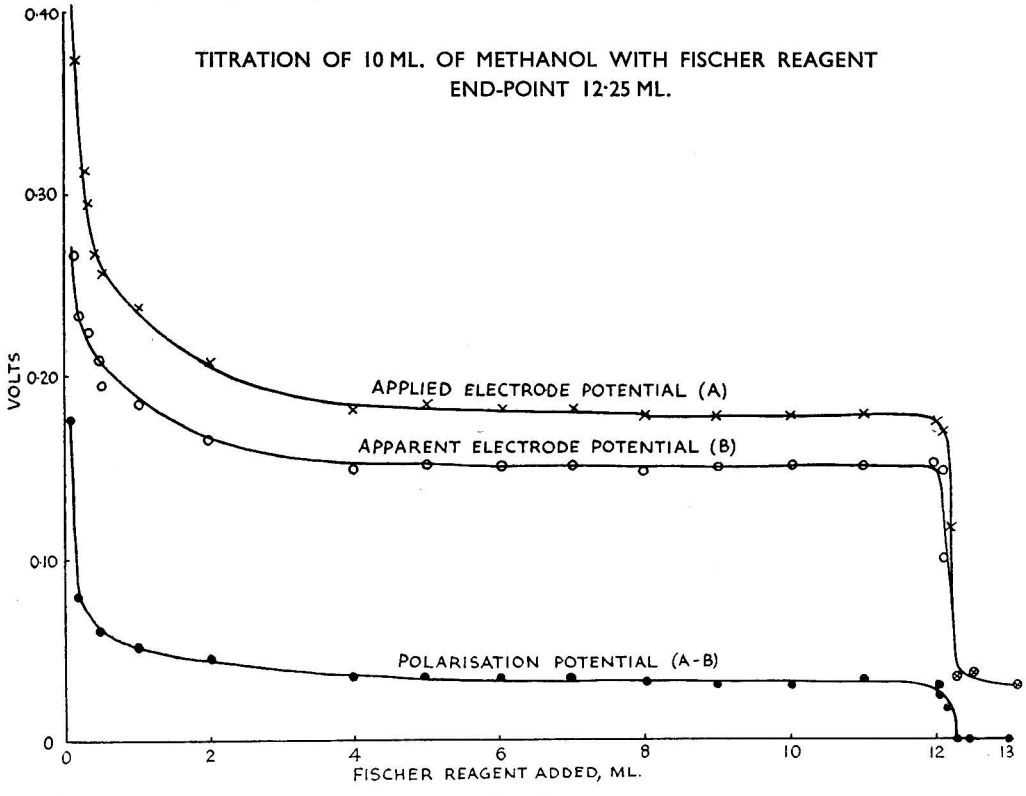

FIG. 2

CONCLUSION

It is suggested that electrometric methods of most types are bound to become a routine procedure in the future and not remain isolated as a special technique by a special operator. Simplification of apparatus and compactness of set-up will help greatly towards making the methods more suitable for general use, and in this respect it is pleasing to note that compact commercial titrimeters are now becoming available. It may be that bi-metallic electrode methods and polarisation end-point methods will find increasing application where possible. In view of the high degree of accuracy often obtainable with electrometric methods it is essential that these methods, where practicable, be utilised as readily as other standard analytical procedures and not be regarded merely as an extraordinary measure when other alternatives fail.

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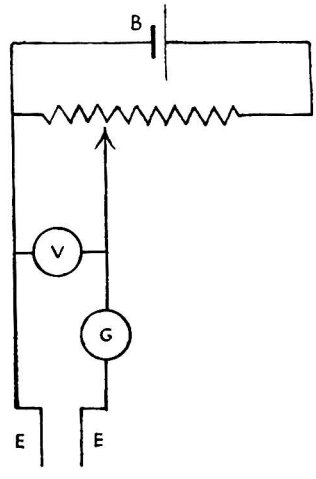
Polarisation End-points

BY D. P. EVANS

IN the three main methods of determining end-points in volumetric analysis, use is generally made of either (1) indicators, (2) an indicator electrode together with a reference electrode, or (3) polarised electrodes. When indicators are employed we usually obtain a rapid and accurate titration in clear colourless liquids but difficulties occur with coloured and turbid liquids, and for routine work in artificial light the possibility of eye-strain cannot be overlooked. In the more usual electro-titrations a salt bridge is necessary between the solution containing the indicator electrode and the standard half-cell. This objection (*i.e.*, the use of a salt bridge) may, however, be obviated by use of a glass electrode as the standard, provided that the *p*H does not alter appreciably during titration. But both methods involve the use



E E denote the two platinum wire or plate electrodes immersed in the test solution, which is provided with a mechanical stirrer.

G is a reflecting galvanometer (sensitivity 22 cm. per micro-amp.).

V is a millivoltmeter.

B represents a small dry battery.

Fig. 1.

of fairly elaborate and expensive apparatus and it is necessary to wait for equilibrium to be reached before accurate readings may be obtained.

The third method depends on the polarisation or depolarisation of one or two inert electrodes at the end-point. The idea was investigated in some detail by van Name and Fenwick,[1] and later by Foulk and Bawden.[2] The latter authors suggested a very simple and inexpensive apparatus which gives surprisingly accurate results under the correct conditions. The other advantages of the method consist in the very rapid—practically instantaneous—development of equilibrium, and the possibility of its use in turbid and coloured solutions.

When an external potential is applied to two platinum electrodes immersed in an acid solution, a back e.m.f. is developed due to deposition of a thin layer of hydrogen on the cathode and one of oxygen on the anode. If the applied e.m.f. is appreciably less than the maximum back e.m.f. of the system, the current in the circuit soon falls to zero. Usually in the polarisation end-point method an e.m.f. of about 10 to 20 millivolts is applied and the galvanometer registers zero current instantaneously. The circuit is illustrated in Fig. 1 on p. 99.

In order to illustrate the method its application to the titration of thiosulphate with iodine will be described. When the electrodes are immersed in a solution of thiosulphate and the applied e.m.f. is switched on, the galvanometer immediately registers zero (or almost zero) current because the back e.m.f. immediately becomes equal to the applied e.m.f. Owing to the reducing action of thiosulphate anions, however, the oxygen is completely removed from the anode and the whole of the back e.m.f. is due to polarisation of the cathode. On addition of a little iodine, the galvanometer spot makes a temporary excursion from the zero position, owing to partial depolarisation of the cathode. The hydrogen thus removed is rapidly replaced and the spot returns to zero. At the end-point, however, the presence of the slightest excess of iodine causes a permanent small depolarisation of the cathode and the applied e.m.f. is then greater than the maximum back e.m.f. which may be developed and the galvanometer registers a small deflection due to current moving in the appropriate direction. Further addition of iodine results in a larger deflection of the galvanometer spot.

If the thiosulphate is added to the iodine there is at first a current which becomes zero at the end-point, hence the term "Dead-Stop End-Point." For accuracy the former method is better.

There is one essential condition for success in the above titration, *viz.*, the anode must be completely depolarised throughout the titration. Two substances can depolarise the anode

(i) Thiosulphate anions:

$$2S_2O_3'' + H_2O + O \longrightarrow S_4O_6'' + 2OH'$$

(ii) Iodide ions:

$$2I' + H_2O + O \longrightarrow I_2 + 2OH'.$$

In 0·1 *N* solutions of iodine there is sufficient potassium iodide to ensure the above condition even at the end-point, but with 0·002 *N* solution, as in the determination of dissolved oxygen in boiler-feed water, as suggested by Hewson and Rees,[3] this is not so. Near the end-point, in the absence of sufficient iodide ions, the accidental current which passes on addition of each drop of iodine to the thiosulphate solution causes polarisation of the anode, with the result that the "back e.m.f." may rise slightly above the applied e.m.f. An amount of iodine somewhat greater than the equivalent must then be added to depolarise the cathode sufficiently to give a current in the direction required by the end-point condition: applied e.m.f. > back e.m.f.

The following table shows the effect of added 10 per cent. potassium iodide solution on the titre of 0·002 *N* iodine dissolved in 0·04 per cent. iodide solution required by 1 ml. of 0·002 *N* thiosulphate in 250 ml. of water.

Experiment No.	Potassium iodide solution added	Iodine titre
	ml.	ml.
1	0·0	1·16
2	0·5	1·08
3	1	1·06
4	2	1·07
5	4	1·01
6	5	1·01
7	10	1·00

When 5 ml. of potassium iodide solution are added the end-point is given accurately even at the dilution employed (1 ml. of 0·002 *N* in 250 ml. of water). Under these conditions starch is totally inadequate as an indicator, yet the polarisation end-point affords an accuracy of ±0·01 ml. of 0·002 *N* I_2 or ±0·0005 ml. of oxygen per litre—an essential requirement when the oxygen content of the boiler feed water must be less than 0·02 ml. per litre (*cf.* Evans and Simmons[4]).

Other applications consist in the measurement of chlorine in domestic water supplies, water in oils, and other oxidation - reduction reactions.

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DISCUSSION

following the reading of the preceding three papers

Mr. C. H. R. GENTRY remarked that although the Cambridge *p*H meter will enable readings to be made to 0·01 *p*H unit, he doubted if it was justifiable to report *p*H measurements to this degree of precision. Co-operative studies made in America appeared to indicate that the accuracy of *p*H measurements with the glass electrode is nearer 0·05 unit. Those studies were made on buffer solutions, and as in practice measurements are often made on poorly buffered, poorly poised solutions a direct-reading *p*H meter measuring to 0·1 unit would probably suffice in industrial analyses. The speaker had found that the "magic eye" in commercial potentiometric apparatus had much to recommend it; with a little care e.m.f.'s could be read with it to within 2 millivolts—a value comparable with that given by galvanometer-type instruments.

Mr. LAUCHLAN pointed out that 2 millivolts correspond to nearly 0·05 *p*H, hence his preference for the galvanometer.

Mr. J. JACKSON said Mr. Gentry might be interested in a semi-statistical examination of the accuracy of commercial glass electrode *p*H meters carried out in America, and reported in *J. Assoc. Off. Agric. Chem.*, 1942, **25**, 973–980 (see also *Ibid.*, 1945, **28**, 579). The method was to send out from a central laboratory bottles of solids, the contents of which were dissolved in distilled water at the receiving laboratory, and the *p*H of the solution was measured, a prescribed solution being used to standardise the *p*H meter. The standard deviation of the accepted results was 0·02 to 0·03 *p*H units. The speaker agreed with Mr. Lauchlan, however, that with careful use the reproducibility of the e.m.f. of a glass electrode cell is considerably better than this figure suggests.

Mr. Carter had referred to the increasing use of *p*H measurements in non-aqueous media. When an ordinary reference electrode is used difficulties are occasionally encountered owing to precipitation at the liquid junction. For example, this occurs with solutions of synthetic resins in mixtures of toluene and ethyl alcohol. It is best then to use a reversible electrode and salt bridge solution, employing an appropriate solvent. Frumkin, in connection with electro-capillary measurements, has described reversible electrodes in a number of alcoholic and other media (*Z. phys. Chem.*, 1922, **103**, 43).

The speaker expressed interest in the chlorine-in-water meter described by Dr. Evans. Presumably what is measured by it is the diffusion current of chlorine to the noble metal electrode, maintained at a constant potential. This current, however, is very susceptible to impurities adsorbed on and in the neighbourhood of the electrode surface. Wallace and Tiernan have patented one or two quite intricate devices to maintain a clear electrode surface in such an instrument. He would like to ask Dr. Evans if the one he described does hold its calibration.

Dr. EVANS replied that it does.

Spot-tests for the Detection of Alloying Elements in Zinc-Base Alloys*

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

THE mechanical properties of zinc-base alloys are such that only a few have been found suitable for general purposes. The usual elements alloyed with zinc are aluminium, copper and lead. Aluminium solders of the zinc-base type have occasionally been employed in industry; these, unlike the constructional alloys, have a variety of alloying elements. Sometimes binary alloys are used for the purpose of soldering but there have appeared alloys of quite complex compositions. The tests to be described in this paper have been designed to be applicable to all the commercial zinc-base alloys.

As far as possible, tests described in previous papers[1,2] have been used, with suitable modifications where necessary and with no needless departure from the usual technique. Some new techniques and reagents, however, have become necessary.

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

Very few samples have been available for the evolution of these tests; the majority have been made and analysed by one of the authors. Whilst every effort has been made to make the tests universally applicable, no guarantee can be given that they will work with alloys of a complex character that have not been encountered in the course of this investigation.

Apparatus—The requirements for these tests are (*a*) short lengths of narrow glass tubing drawn out into long fine jets, (*b*) stirring rods similarly drawn out into points, (*c*) a few small watch-glasses of about two inches diameter, (*d*) 400-ml. squat beakers on which to support the papers of tests (II) and (VI), (*e*) a small dish 2 inches in diameter and 1·5 inches deep, (*f*), white porcelain tile and (*g*) Petri dishes of about 6 inches diameter.

THE TESTS—The samples must be cleaned by rubbing with an emery paper of fairly coarse texture before the tests are applied.

In all but one of the following tests the reaction products have to be removed from the surface of the sample for completion of a test; this is due to the highly reactive nature of the base metal. In two instances, those of tin and lead, addition of aluminium in the form of small chips or coarse powder to the surface before adding the attacking reagent has been found necessary. This innovation facilitated solution of the tin from the alloy and, in the case of lead, left on the metal a loose deposit which could be easily separated from the base metal for subsequent treatment.

Compositions of trial alloys are given in the Appendix (page 105), and the numbers at the end of each test refer to that Appendix.

(I) COPPER

Reagents—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Mixture of α-benzoin-monoxime in alcohol (saturated solution), 10 vols.; diluted ammonia (1+1), 20 vols.; citric acid solution (50 per cent.), 5 vols.
(*c*) Hydrogen peroxide (20 vol. solution).

Method—Add 1 drop of (*a*) to the thoroughly cleaned surface and leave it to react for 1 to 2 minutes. Then add 6 drops of (*b*), stir well, follow with 1 drop of (*c*) and stir again. In presence of copper a dirty green precipitate quickly develops. In absence of copper there may be a slight white precipitate due to the reagent.

Tried on: Samples Nos. 8, 1, 9—Copper present; all gave positive results.
Nos. 2, 4, 5, 6, 7—Copper less than 0·10 per cent. and all results negative.

(II) ALUMINIUM

Reagents—(*a*) Hydrochloric acid (5 per cent. solution) saturated with bromine.
(*b*) Mixture of sodium hydroxide solution (20 per cent.), 1 vol.; potassium cyanide solution (10 per cent.), 1 vol.
(*c*) Ammonium chloride solution (20 per cent.).
(*d*) Ammonium aurintricarboxylate solution (0·1 per cent.) in alcohol.

Method—Prepare a disc of fairly close-grained filter-paper by running on to it 1 ml. of (*d*), causing the liquid to spread as evenly as possible and allowing to dry; lay the prepared paper on the open mouth of a beaker. Place on the thoroughly cleaned sample 1 drop of (*a*) and allow it to become decolorised. Add 4 or 5 drops of mixture (*b*) and stir thoroughly. Transfer the liquid, by means of a capillary tube, to the centre of the paper in a dropwise manner. When the last drop has been completely absorbed lay the paper flat on a clean tile and cover it with a piece of filter paper which has been soaked in (*c*) and allowed to drain. Allow the covering paper to remain in position for a few seconds, then strip off, return the other paper to the top of its beaker and leave for 15 minutes. Wash the paper about 6 times with 3 or 4 drops of (*c*), dropped into the centre and allowed to spread before the next wash is added, and then leave to dry.

Aluminium is indicated by a scarlet ring, about 1½ to 2 inches from the centre, sharply defined on the inner and somewhat diffused on the outer side; it is usually ⅛ to ¼ inch broad. The ground within the ring should be white, that outside generally a purplish band of the dye itself. The record on the paper seems to be quite stable and, after drying, will keep indefinitely.

Tried on: Samples Nos. 5, 9, 1, 2, 8, 3, 6—Aluminium present; all gave positive results.
Nos. 4, 7—Aluminium absent and both results negative.

(III) Antimony

Reagents—(*a*) Mixture of tartaric acid solution (50 per cent.), 1 vol.; saturated bromine water, 1 vol.
(*b*) Hydrochloric acid solution (10 per cent.).
(*c*) Sodium hypophosphite (solid).
(*d*) Copper foil (approximately 3/16 inch square).

Method—Place 6 drops of (*a*) on the thoroughly cleaned surface and allow to react until the bromine colour has nearly disappeared; quickly wash the drops into a 60-ml. tall-form beaker, with a few drops of water. Add 10 ml. of (*b*) to the reaction drops and then about 0·5 g. of (*c*) and the piece of copper foil (*d*), previously cleaned with nitric acid, taking care not to touch the copper foil with the fingers. Boil the solution gently until the salts begin to crystallise and the volume of the liquid is about 0·5 to 1 ml.; then cool and dilute with water. With small quantities of antimony it is only after the salts begin to crystallise that the antimony deposits on the copper. Place the beaker on a white glazed tile for comparison with a blank test carried out under exactly the same conditions; comparison should be made by looking vertically downwards on to the beakers.

Only one sample containing antimony was available, *viz.*, No. 6; this gave a positive reaction.

Tried on: Samples Nos. 1, 2, 4, 5, 7, 8, 9—Antimony absent and all results negative.

(IV) Tin

Reagents—(*a*) Mixture of tartaric acid solution (50 per cent.), 4 vols.; diluted nitric acid (sp.gr. 1·20), 2 vols.; potassium cobalticyanide solution (10 per cent.), 1 vol.
(*b*) Mixture of diluted hydrochloric acid (15 per cent. v/v), 4 vols.; potassium cobalticyanide solution (10 per cent.), 1 vol.
(*c*) Mixture of toluene-3:4-dithiol[3] solution (0·5 per cent.) in water-free acetone (prepared fresh daily), 1 vol.; thioglycollic acid solution (0·5 per cent.) in acetone, 1 vol.
(*d*) Aluminium chips or coarse powder.

Method—To the thoroughly cleaned surface add a small quantity of (*d*) followed by 4 drops of (*a*), mix-in the aluminium and then leave to react for 5 minutes. Add 6 drops of (*b*), stir, and leave for 1 to 2 minutes. Transfer the solution to a watch-glass either by means of a capillary tube, or by tilting the sample so that the liquid runs on to the watch-glass. Add 4 drops of (*c*), stir and leave to react. In presence of tin the white precipitate that first forms turns red slowly. In absence of tin the colour of the precipitate varies from a pale yellow to a grey; the yellow is due to zinc (and cadmium if present) both of which slowly fade to a dirty white; the grey colour is due to copper, not precipitated by the cobalticyanide, giving a black precipitate with the reagent.

In presence of large amounts of copper the greater part of the tin present is co-deposited as the copper - tin compound[4]; sufficient remains in solution, however, to give a strong reaction. If, after the bulk of the liquid has been removed from the sample as described above, the remaining liquid is allowed to dry and the crust removed by scraping with a knife or razor blade, a considerable reaction for tin is given when the crust is treated with the reagents as described in the test.

Tried on: Samples Nos. 6, 8, 9—Tin present; all gave positive results.
Nos. 7, 4, 5, 1, 2—Tin absent and all results negative.

(V) Cadmium

Reagents—(*a*) Mixture of diluted nitric acid (sp.gr. 1·20), 1 vol.; citric acid solution (50 per cent.), 1 vol.
(*b*) Mixture of diluted ammonia (1+1), 1 vol.; ammonium nitrate solution (20 per cent.), 1 vol.
(*c*) Mixture of potassium cyanide solution (20 per cent.), 3 vols.; sodium sulphide solution (10 per cent.), 1 vol.

Method—To the thoroughly cleaned surface add 2 drops of (*a*) and leave until the vigorous reaction has ceased; wash the drop off the sample, by means of a fine jet of distilled water, on to a watch-glass. Add 4 drops of (*b*), stir, then add 6 drops of (*c*), stir again and leave for

the cadmium sulphide precipitate to develop. In absence of cadmium the mixed drops remain clear. Cadmium gives a bright yellow precipitate. A series of zinc - cadmium alloys were prepared containing amounts of cadmium from 20 per cent. down to 1 per cent.; all gave visible yellow precipitates, although those from the 2·5 per cent. and 1·0 per cent. solutions were rather slow in forming.

Tried on: Samples Nos. 7, 10, 11, 12, 13, 14—Cadmium present; all gave positive results.
Nos. 8, 9, 4, 5, 6, 1, 2—Cadmium absent and all results negative.

(VI) Lead

Reagents—(*a*) Diluted nitric acid solution (sp.gr. 1·20).
(*b*) Concentrated hydrochloric acid saturated with bromine.
(*c*) Diluted ammonia (1+1).
(*d*) Mixture of ammonium acetate solution, 2 vols.; sodium chromate solution (5 per cent.), 1 vol. To prepare the ammonium acetate solution, add to 1140 ml. of distilled water in a 3-litre porcelain beaker placed in a cooling bath 500 ml. of concentrated ammonia (sp.gr. 0·880) followed by 570 ml. of glacial acetic acid, with continuous stirring, and allow to cool; the solution should be neutral.
(*e*) Mixture of potassium cyanide solution (5 per cent.), 9 vols.; dithizone solution (0·1 per cent.) in chloroform, 1 vol.
(*f*) Aluminium chips or coarse powder.
(*g*) Acetone.

Method—Place a small quantity of (*f*) on the thoroughly cleaned surface, add 4 drops of (*a*), stir-in the aluminium and leave to react for 5 minutes. Transfer the drops, by means of a capillary tube, to a watch-glass. Remove the aluminium from the surface of the sample by washing with acetone and then leave to dry. Carefully remove the deposit from the surface of the sample, by means of a sharp knife or razor blade and drop it on to the liquid already on the watch-glass. Add 3 drops of (*b*) and stir with a pointed glass rod, until all is dissolved. Place a 9-cm. No. 541 Whatman filter paper on the open mouth of a beaker, transfer the solution from the watch-glass on to the centre of the paper and allow it to spread. Place the paper on top of a dish, of about 2 inches diameter, containing (*c*) and leave, covered, for 1 minute, by which time all the free acid should be neutralised. Transfer the paper to a Petri dish containing (*d*), allow it to soak for a few seconds and then remove and drain it for 30 seconds. Next wash the paper for 2 to 3 minutes in running water, transfer it to a second Petri dish containing (*e*) and develop, with occasional agitation, for 15 minutes; again wash in running water until the colour of the paper has changed from golden brown to a light pink and hang it up to dry. Lead is indicated by a red patch covering the whole of the original wet area; sometimes there is a tendency for the lead to accumulate, forming a ring of denser colour at the outer edge. The rest of the paper should be white, or a very pale shell-pink, when dry. In absence of lead the paper is white or a uniform pale shell-pink.

Reagent mixture (*e*) should be thoroughly mixed before use, the cyanide having a golden colour; when the chloroform layer begins to appear brownish, instead of its usual black colour when freshly prepared, it is an indication that the mixture (*e*) should be renewed.

Tried on: Samples Nos. 6, 7, 8, 9—Lead present; all results positive.
Nos. 1, 2, 4, 5, 10, 11, 12—Lead absent and all gave negative results.

Note—The presence of lead in sample No. 7 was discovered by this test; subsequent analysis showed that the sample contained 0·26 per cent., and that the cause of its introduction into the alloy was the supposedly pure cadmium. Alloys Nos. 10–14 were prepared from pure zinc and cadmium.

Summary

Tests are described for the detection of alloying elements in zinc-base alloys. The alloying elements so detected are copper, aluminium, antimony, tin, cadmium and lead.

With the alloys at our disposal the tests were found to be specific and unambiguous.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

APPENDIX

SPECIMENS OF ALLOYS USED IN THE TESTS. CONSTITUENTS PER CENT.

No.	Mark	Al	Cu	Pb	Mg	Fe	Sb	Sn	Cd	Remarks
1	210	4·30	1·01	—	0·054	0·01	—	—	—	
2	209	4·14	0·03	—	0·052	0·008	—	—	—	
3	L/AUW	4·05	0·003	0·004	0·05	—	—	—	—	
4	Zinc	—	—	—	—	—	—	—	—	
5	JQW	21·5	—	—	—	—	—	—	—	Made up and analysed by one of the authors. No. 6 is of nominal composition only.
6	DKL(N)	0·25	0·05	1·5	—	—	0·15	18·5	—	
7	EX.8	—	—	0·26	—	—	—	—	44·0	
8	EX.10	3·80	2·18	0·74	—	—	—	24·0	—	
9	EX.9	15·0	0·84	0·43	—	—	—	6·53	—	
10	EX.69	—	—	—	—	—	—	—	20	Nominal composition only; not actually analysed.
11	EX.70	—	—	—	—	—	—	—	10	
12	EX.71	—	—	—	—	—	—	—	5	
13	EX.72	—	—	—	—	—	—	—	2·5	
14	EX.73	—	—	—	—	—	—	—	1·0	

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Spot-tests for the Detection of Alloying Elements in Lead-base Alloys*

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

LEAD-BASE alloys have found extensive application in industry, with the result that there is a wide range of alloying elements. Specifications[1] for these alloys include the elements tin, antimony, cadmium, silver, arsenic, bismuth and tellurium in various percentages and admixtures. The samples used in the course of developing these tests have been made up either from the above-mentioned specifications, or from alloys previously analysed in this laboratory; all have been analysed by one of the authors.

Tests are described for the following elements: tin, antimony, cadmium, silver, arsenic and bismuth. Except those for bismuth and cadmium, which are modifications of tests described in an earlier paper,[2] the tests described are entirely new to our programme of spot-testing. The antimony test is a departure from the Reinsch test, to which we have strictly adhered in former papers.[2,3,4] The Reinsch test, although very reliable and delicate, is not well suited to the detection of antimony in lead-base alloys. Clarke's[5] modification of the Reinsch test permits the presence of large amounts of tin but, as difficulty might be encountered from arsenic and high bismuth contents, the method has not been tested. The test described for the detection of arsenic is a modification of Gutzeit's test. Numerous tests tried for the detection of tellurium were all unsuccessful; it is our opinion that the amount specified under S.T.A.7 or B.S.334, Type B (0·06 to 0·07 per cent. of copper; 0·04 to 0·05 per cent. of tellurium) is below the limits of detection.

Apparatus—In addition to the droppers, stirrers and capillary tubes, already described in former papers, the following are needed: (*a*) white porcelain spot-plate, (*b*) tile or glass plate covered with black paper (used in Test IV, Silver), (*c*) apparatus used for the arsenic test (*vide* Test V) and (*d*) metal scraper for cleaning the sample.

Owing to the surface plastic flow of lead when treated with light pressures, the use of emery paper for polishing is very unsatisfactory; resort has to be made to the use of a scraper. The instrument employed throughout these tests was made from a wooden-handled steel spatula. The steel blade was cut off square about 2¼ inches from the hilt. The end of the

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

blade was made red-hot and, while still hot, bent at right angles about $\frac{1}{4}$ inch from the end of the blade. When cool, the surface of the edge facing the handle was ground to form a sharp cutting-edge. The blade was first cleaned with emery paper to present a bright surface and then heated over a small flame until the whole of the part at right angles to the handle became of a straw-yellow colour and the last $\frac{1}{8}$ of an inch varying from light blue to deep blue at the cutting edge; it was then allowed to cool. By pressing the blade on the specimen and drawing it backwards a clean, smooth surface was obtained.

THE TESTS—Of the tests described only two can be carried out completely on the surface of the sample—they are those for tin and bismuth; the tests for antimony, cadmium, silver and arsenic require removal of the reaction drops at some intermediate stage for completion.

(I) TIN

Reagents—(*a*) Mixture of diluted nitric acid (sp. gr. 1·20), 1 vol.; tartaric acid solution (50 per cent.), 1 vol.
(*b*) Diluted hydrochloric acid (15 per cent. v/v).
(*c*) Mixture of toluene-3:4:-dithiol[6] solution (0·5 per cent.) in water-free acetone, prepared fresh daily, 1 vol.; thiogylcollic acid solution (0·5 per cent.) in acetone, 1 vol.

Method—To the thoroughly cleaned surface add 2 drops of (*a*) and leave to react for 5–10 minutes; then add 4–5 drops of (*b*) followed by 3–4 drops of (*c*), stir, and leave to react. In presence of large amounts of tin an immediate red precipitate is observed, with about 5 per cent. of tin the development of the precipitate is somewhat delayed and, for 0·5 per cent. of tin at least 5–10 minutes may be required before the colour develops. Bismuth does not give its reddish-brown precipitate under the conditions of the test. In absence of tin all other alloys give either varying shades of yellow or no precipitate at all. The reactions are somewhat less intense when silver is present in the alloy, *e.g.*, there does not appear to be much difference in intensity between the reactions for 5 per cent. and 50 per cent. of tin.

Tried on: Samples Nos. 18, 17, 19, 10, 20, 15, 21, 7, 23, 24, 25, 26, 27, 28, 29, 30—Tin present; all results positive.
Nos. 22, 31, 2, 4, 6, 8, 9, 13, 14, 16, 36—Tin absent and all results negative.

(II) ANTIMONY

Reagents—(*a*) Concentrated hydrochloric acid saturated with bromine.
(*b*) Concentrated hydrochloric acid.
(*c*) Potassium nitrite (solid).
(*d*) Rhodamine "B"[7] solution (0·01 per cent.) in water.

Method—Add to the thoroughly cleaned surface 3 drops of (*a*) and allow to react until the bromine colour has just become dispelled. Withdraw the drop, by means of a capillary tube, together with as much of the white oxide precipitate as possible (this precipitate results from high antimony contents) and place it in a well of a white porcelain spot-plate. Add 2 drops of (*b*), stir and follow with a few small crystals of (*c*), stir again and then leave for about 1 minute. Add 4 drops of (*d*) to another well of the spot-plate, transfer 2 drops from the first well to the reagent and stir thoroughly. In presence of antimony in proportions down to about 1·5 per cent. an immediate purple coloration is observed. Antimony contents of about 0·5 per cent. give a purple-mauve reaction which fades rapidly if the tin content of the sample is high. In presence of silver, all antimony contents give the reaction, but all are subject to somewhat rapid fading. With lead - antimony alloys a strong purple-mauve reaction is given by 0·25 per cent. of antimony. In absence of antimony the colour of the drop varies from a dirty brick-red to a reddish pink.

Tried on: Samples Nos. 1, 2, 6, 7, 8,9, 11, 13, 15, 16, 17, 18, 19, 20, 21, 25, 26, 28, 29, 33, 34, 32—Antimony present; all gave positive results.
Nos. 4, 10, 14, 22, 24, 27, 30, 31, 36—Antimony absent and all results negative.

(III) CADMIUM

Reagents—(*a*) Diluted nitric acid (sp.gr. 1·20).
(*b*) Potassium cobalticyanide solution (10 per cent.).
(*c*) Mixture of cobalticyanide solution (10 per cent.), 1 vol.; nitric acid solution (sp.gr. 1·20), 1 vol.

(*d*) Mixture of diphenylcarbazone solution (1·5 per cent.) in alcohol, 1 vol.; saturated borax solution, 1 vol.*
(*e*) Half-saturated borax solution.
(*f*) Ethyl alcohol.

Method—Attack the cleaned surface with 2 drops of (*a*) and allow to react for 3–4 minutes; then add 2 drops of (*b*), stir, and leave for 1 minute. Remove the drops, by means of a capillary tube, and drop them on to the centre of a fine-grain filter-paper, supported on the open mouth of a beaker, allowing each drop to become completely absorbed before adding the next. When all the transferred liquid has been added to the paper and the last drop has completely soaked in, add 2 drops of (*c*); when this has disappeared follow with two 2-drop washings of (*b*), again allowing each wash to disappear before adding the next. Add 3 drops of (*d*) and leave to spread; it is important for the following reactions that the last drop of (*b*) should have completely disappeared before addition of (*d*). Continue by washing the reagent patch with two 4-drop washings of (*e*). Finally add to the centre of the reagent patch, in a slow dropwise manner, 4 drops of (*f*); allow to finish spreading, then add a further two 4-drop washings and leave until dry. When dry the paper will show, if cadmium is present, a dark purple irregular ring, about 1½ to 2 inches in diameter, just inside the outer mauve edge of the reagent patch. With cadmium contents of, say, 0·18 per cent., this dark purple ring may not be more than a line. In absence of cadmium the outer edge of the reagent patch forms a mauvish-purple band, about ¾ inch wide, but no sign of the dark purple irregular ring appears.

Tried on: Samples Nos. 3, 4, 5, 6, 7, 11, 12—Cadmium present: all gave positive results.
Nos. 2, 8, 13, 14, 15, 16, 18, 22, 36—Cadmium absent and all results negative.

(IV) Silver

Reagents—(*a*) Dlluted nitric acid (sp.gr. 1·20).
(*b*) Potassium cyanide solution (20 per cent.).
(*c*) Ammonium acetate solution, 4 vols.; potassium iodide solution (4 per cent.), 1 vol.; acetic acid (glacial), 1 vol. To prepare the ammonium acetate solution, add to 1140 ml. of distilled water in a 3-litre porcelain beaker placed in a cooling bath 500 ml. of concentrated ammonia (sp.gr. 0·880) followed by 570 ml. of glacial acetic acid, with continuous stirring, and allow to cool; the solution should be neutral.

Method—To the thoroughly cleaned surface add 2 drops of (*a*) and allow to react for 5 minutes. Remove the excess of acid by touching the edge of the drop with the end of a capillary tube. To the wet patch resulting from the previous operation add 3 drops of (*b*), stir thoroughly and then leave for 5 minutes. Transfer the cyanide drop from the sample to a small watch-glass; this is best done by placing a capillary tube at the edge of the drop and tilting the sample slightly, the object being to effect removal of the liquid (together with some lead cyanide) without disturbing any of the black metallic deposit which adheres loosely to the sample. Place the watch-glass, containing the transferred cyanide drops, on a black background (*vide* Apparatus (*b*), page 105). Add 6–8 drops of (*c*), stir well until all the lead cyanide has dissolved, then leave for 15 minutes. In presence of silver an immediate pale yellow precipitate or whitish yellow haze is produced; in both instances the silver iodide may be accompanied by metallic silver, giving the drop a dark appearance. The halide precipitate, or haze, is clearly seen against the black background. In absence of silver all samples give a *clear*, colourless solution.

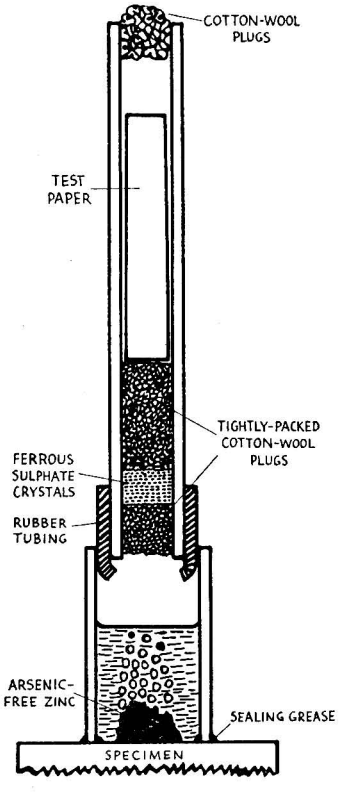
Tried on: Samples Nos. 22, 23, 24, 25, 26, 27, 28, 29, 30—Silver present; all gave positive results.
Nos. 2, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 31, 36—Silver absent and all results negative.

(V) Arsenic

Reagents—(*a*) Diluted hydrochloric acid (1+1) saturated with bromine.
(*b*) Concentrated hydrochloric acid.
(*c*) Arsenic-free zinc.
(*d*) Mercuric chloride test paper.
(*e*) Ferrous sulphate (small crystals).

* The addition of the borax solution to the alcoholic reagent results in deposition of some of the borax; it is advisable to decant the supernatant liquid for use in the test.

Apparatus—See Figure. It comprises (*g*) a glass tube 1 inch long by $\frac{5}{8}$ inch in diameter, ground flat at both ends, (*h*) a narrower glass tube $2\frac{3}{4}$ inches long by $\frac{3}{8}$ inch in diameter, fitted at one end with a half-inch length of rubber tubing, a little of which overlaps the end of the glass tube (*h*), forming a slightly tapered end that serves as a stopper fitting snugly into tube (*g*), (*j*) rubberised vaseline such as is used for stop-cock lubricants and (*k*) cotton-wool.



To prepare the tube (*h*) for the test, insert a tightly packed plug of cotton-wool into the tube so that its lower end is about 0·5 inch from the bottom of the tube, the plug being about 0·5 inch deep. To the rubber-tubing end of the cotton-wool add fine crystals of (*e*) until a layer about $\frac{1}{4}$ inch thick has been formed; then insert a second cotton-wool plug to prevent the ferrous sulphate from falling out when the tube is in position for the test. Cut a strip of paper (*d*) about $\frac{1}{4}$ inch by $1\frac{1}{4}$ inch, insert it in the glass tube and then plug the free end of the tube loosely with cotton-wool; the tube is now ready for the test. (See Figure.)

Method—Scrape the specimen until the surface is both clean and flat. Dip the end of the glass tube (*g*) into the hot sealing grease (*j*), then withdraw it and, after making sure that there is no bubble film of grease across the end of the tube, press it firmly on to the sample. Add 4 drops of (*a*) inside the wide tube (*g*) and leave to react for 5 minutes. Add 15 drops of (*b*) inside the wide tube. Drop a small granule of (*c*) into the wide tube and allow the reaction to proceed for a few seconds; then, before the bromine has been destroyed, insert the rubber-stoppered end of the prepared tube (*h*) and leave for 15 minutes. Detach the top tube (*h*), remove the top plug and shake out the test strip. If arsenic is present there will be a yellow, orange or brown coloration of the middle part of the strip. If the alloy contains notable amounts of antimony the whole of the strip will have been covered with a brown or black coloration shortly after all the bromine has been destroyed. The coloration immediately begins to fade and at the end of the 15 minutes only the lower end of the strip remains coloured. On exposure to air and light for 1 hour the antimony stain is reduced to a light grey stain or coloration at the base of the strip, whilst the arsenic stain will be plainly visible on the middle portion of the strip. Antimony contents of 2 to 3 per cent. give a slight yellow coloration at the base of the strip but this fades completely after a short exposure to the air. All other samples, not containing arsenic or high antimony, showed no coloration of the paper throughout the test.

Tried on: Samples Nos. 1, 2—Arsenic present: both gave positive results.
Nos. 8, 13, 15, 20, 25, 16, 9, 4, 6, 7, 10, 12, 14, 18, 22, 24, 28, 30, 31, 36—Arsenic absent and all results negative.
Nos. 8, 13, 15, 20, 25, 16, 9—All contain more than 7·0 per cent. of antimony and all gave the reaction described in the test above; it could in no case be confused, however, with the reaction given by arsenic.

(VI) Bismuth

Reagents—(*a*) Mixture of diluted nitric acid (sp.gr. 1·20), 1 vol.; tartaric acid solution (50 per cent.), 1 vol.
(*b*) Urea solution (10 per cent.).
(*c*) Mixture of potassium iodide solution (4 per cent.), 1 vol.; antipyrine solution (1 per cent.) in water, 2 vols.
(*d*) Sodium thiosulphate solution (2·5 per cent.).

Method—Add 2 drops of (*a*) to the thoroughly cleaned surface and leave to react for 2 to 3 minutes. Add 4 drops of (*b*), stir, then follow with 3 drops of (*c*) and stir again; add 2 drops of (*d*) and stir the whole thoroughly. In presence of bismuth an orange-brown

precipitate will be observed, whilst in absence of bismuth a yellow precipitate of lead iodide is formed. If the amount of reagent (*b*) is just insufficient to destroy all the nitrous acid formed a slow liberation of iodine discolours the drop, simulating the bismuth reaction; the two drops of (*d*) added completely destroy the liberated iodine, leaving the lead iodide of a bright yellow colour if bismuth is absent.

Tried on: Samples Nos. 8, 9, 14, 15, 16—Bismuth present; all gave positive results.
Nos. 2, 6, 10, 13, 18, 20, 22, 30, 31, 36—Bismuth absent and all results negative.

SUMMARY

Tests are described for the detection of alloying elements in lead-base alloys. The alloying elements so detected are tin, antimony, cadmium, silver, arsenic and bismuth.

With the alloys at our disposal the tests are specific and unambiguous. The amounts of tellurium present in commercial alloys are too low to permit a spot test.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

APPENDIX

SPECIMENS OF ALLOYS USED IN THE TESTS. CONSTITUENTS PER CENT.

No.	Mark	Sn	Sb	Bi	Cd	As	Ag	Te	Remarks
1	EX.18	—	2·38	—	—	0·55	—	—	
2	EX.19	—	2·71	—	—	0·97	—	—	
3	EX.20	—	—	—	0·18	—	—	—	
4	EX.27	—	—	—	1·07	—	—	—	
5	EX.28	—	—	—	0·65	—	—	—	
6	EX.29	—	2·0	—	2·10	—	—	—	
7	EX.30	0·50	2·0	—	1·11	—	—	—	
8	EX.31	—	14·46	15·0	—	—	—	—	
9	EX.32	—	7·40	8·17	—	—	—	—	
10	EX.33	32·25	—	—	—	—	—	—	
11	EX.34	—	0·50	—	0·28	—	—	—	
12	EX.35	1·50	—	—	0·26	—	—	—	
13	EX.36	—	12·0	—	—	—	—	—	
14	EX.37	—	—	3·60	—	—	—	—	
15	EX.38	5·46	11·83	4·77	—	—	—	—	
16	EX.39	—	11·50	4·20	—	—	—	—	
17	EX.40	36·80	0·42	—	—	—	—	—	
18	EX.41	42·45	2·64	—	—	—	—	—	
19	EX.42	31·55	1·46	—	—	—	—	—	
20	EX.44	10	20	—	—	—	—	—	Nominal composition only
21	EX.45	5	10	—	—	—	—	—	
22	EX.57	—	—	—	—	—	2·48	—	
23	EX.58	0·95	—	—	—	—	1·36	—	
24	EX.59	4·90	—	—	—	—	1·36	—	
25	EX.60	20·05	9·43	—	—	—	0·53	—	
26	EX.61	24·50	1·52	—	—	—	0·52	—	
27	EX.62	29·22	—	—	—	—	0·57	—	
28	EX.63	31·93	1·77	—	—	—	0·98	—	
29	EX.64	36·16	1·86	—	—	—	1·11	—	
30	EX.65	43·67	—	—	—	—	1·39	—	
31	EX.68	—	—	—	—	—	—	0·068	0·007 per cent. Cu also present
32	EX.74	—	1·00	—	—	—	—	—	Nominal composition only
33	EX.75	—	0·50	—	—	—	—	—	
34	EX.76	—	0·25	—	—	—	—	—	
35	EX.77	25	—	—	—	—	—	—	
36	LEAD	—	—	—	—	—	—	—	

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Notes

THE TITRATION OF MINUTE AMOUNTS OF NICKEL*

AMENDMENT TO THE METHOD PUBLISHED IN "THE ANALYST," 1946, 71, 457

SINCE the publication of this method considerable trouble has arisen in the accurate titration of minute amounts (less than 0·0001 g.) of nickel, high results being obtained. This trouble has been traced to the extraordinary impurity of the amyl alcohol available. As amyl alcohol appears to be a very unreliable substance search was made for a substitute, and it appears that benzene is completely satisfactory.

The following figures were obtained by the same method but with 20 ml. of benzene instead of the original 20 ml. of amyl alcohol. The remaining procedure was the same, *i.e.*, use of

(*a*) 20 ml. of 20 per cent. ammonium nitrate solution.

(*b*) water up to 100 ml.

(*c*) 50 ml. of *N*/5 sodium carbonate (in view of the low amounts).

(*d*) 0·3 ml. of 1·5 per cent. diphenylcarbazone reagent.

(*e*) violent shaking for 15 seconds after each addition and occasional shaking of the blank.

(*f*) a stand of some minutes before the final matching.

Nickel taken mg.	Titration with 100-fold diluted KCN solution ml.	Nickel found mg.
0·0100	1·0	0·0105
0·0200	1·9	0·0200
0·0300	3·0	0·0315
0·0400	3·8	0·0399
0·0500	4·8	0·0504
0·0020	0·2	0·0021

The factor of the undiluted potassium cyanide solution was 1·050. The amount of nickel used in the final titration (only 2 μg.) was lower than anything I had attempted before.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this note.

B. S. EVANS

January, 1947

A SIMPLE METHOD FOR ELECTRIC HEATING

HAVING had occasion to convert some incubators from gas to electric heating, I have found that ordinary mica-insulated electric-iron elements, which are cheap and easily obtainable, are very suitable for the purpose. The method used is to hold them firmly against the water-jacket by means of a piece of asbestos millboard in which slits are cut to take the electrodes. These are soldered to leads, another layer of millboard is placed over the leads, and the whole pressed in contact with the tank by tiles held in a wood or metal framework. I find that for an ordinary incubator or thermostat three, four or even five such units *in series* gives a convenient current (four in series passes about half an ampere). A series-parallel switch gives larger currents for starting-up, if necessary. Working thus with a small load, the life of the elements should be very long.

In these days of delay in getting things done through the usual channels this simple method may have a number of applications in laboratory heating problems.

H. S. HOWES

THE LABORATORY
4, QUEEN SQUARE, BRISTOL, 1

December, 1946

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

EVAPORATION FROM BEAKERS WITH RADIANT HEATER

THE application of the "Vitreosil" radiant heater to evaporation from open dishes is well known. Occasions arise, however, when it is convenient to complete an evaporation in a beaker, under conditions when heating from the top is necessary to avoid spitting. Under ordinary conditions this is very slow, but I have found that it is rapidly accomplished by placing the beaker or beakers in a metal vessel considerably larger than the beaker. Five squat-form 250-ml. beakers can be very conveniently heated simultaneously in this way by placing them under the heater in an aluminium saucepan 9 inches in diameter and 5 inches deep.

H. S. HOWES
December, 1946

THE LABORATORY
4, QUEEN SQUARE, BRISTOL, 1

Ministry of Food

STATUTORY RULES AND ORDERS

1947—No. 162. The Meat Products and Canned Meat (Control and Maximum Prices) Order, 1947. Dated January 30, 1947. Pp. 18. Price 5d.

This is a consolidating Order which substantially re-enacts the Meat Products, Canned Soup and Canned Meat (Control and Maximum Prices) Order, 1946; *S.R. & O., No.* 1355 *of* 1946; ANALYST, 1946, **71**, 382) *as amended (S.R. & O., No.* 1727 *and No.* 2046 *of* 1946; ANALYST, 1947, **72**, 64). *The principal changes are in maximum prices and charges. The restriction on labelling specified foods canned for sale to the Minister of Food has been removed.*

Meat paste and fish paste are not now listed in Schedule I, which is headed "Minimum Meat Content of Specified Foods (not Canned)"; but in Article 10 *the minimum meat content of meat paste is fixed at* 55 *per cent.* (50 *per cent. at discretion, in Court proceedings) and the minimum fish content of fish paste is fixed at* 70 *per cent.* (65 *per cent. at discretion, in Court proceedings*).

In accordance with S.R. & O., No. 2046 *of* 1946, *soups are not now included in the scope of the Order.*

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Seed Oils of some Sudan Caesalpinioideae. D. N. Grindley (*J. Soc. Chem. Ind.*, 1946, **65**, 118–119)—Fatty acids of high molecular weight (20 to 24 carbon atoms) are characteristic of Caesalpinioideae, as of the other Leguminosae sub-families. Constants were determined for the following plants: (i) *Erythrophleon guineense*, a well known poison tree containing as main active principle the alkaloid erythrophleine, $C_{28}H_{43}O_7N$, (ii) *Parkinsonia aculeata*, (iii) *Cassia fistula*, of the British Pharmacopoeia, (iv) *Tamarindus indica*, of the British Pharmacopoeia, and (v) *Cassia arereh*, a small tree of the Fung area. Results obtained are: Saponification values, (i) 190·4, (ii) 190·6, (iii) 184·9, (iv) 181,9, and (v) 192·3; unsaponifiable matter, (i) 2·5, (ii) 6·25, (iii) 5·4, (iv) 3·8, and (v) 2·7 per cent.; n_D^{40}, (i) 1·4661, (ii) 1·4719, (iii) 1·4668, (iv) 1·4667, and (v) 1·4672; iodine values, (i) 98·1, (ii) 114,0, (iii) 94·5, (iv) 94·5, and (v) 93·8; thiocyanogen values, (i) 63·1, (ii) 69·1, (iii) 63·2, (iv) 61·3, and (v) 61·5; m.p. of fatty acids (slip point), (i) 32·5, (ii) 33, (iii) 37, (iv) 45·5 (titre 43°) and (v) 33·5° C. Insoluble fatty acids plus unsaponifiable matter (Hehner value) are (i) 96·1, (ii) 96·3, (iii) 96·05, (iv) 95·6, and (v) 95·3 per cent. The approximate percentage compositions of the mixed fatty acids are: Oleic, (i) 26·8, (ii) 20·6, (iii) 31·9, (iv) 27·3, and (v) 28·7; linoleic, (i) 43·6, (ii) 56·0, (iii) 39·0, (iv) 41·9, and (v) 40·2; saturated acids, (i) 29·6, (ii) 23·4, (iii) 29·1, (iv) 30·8, and (v) 31·1; higher saturated acids, (C_{20} to C_{24}), (i) 1·6, (ii) 1·0, (iii) 4·8, (iv) 11·8, and (v) 4·4. The oil contents of the seeds are (i) 5·60, (ii) 1·65, (iii) 2·04, (iv) 4·33, and (v) 5·54 per cent. All the oils are highly coloured. The higher acids of (iv) had mean molecular weight of 374 and m.p. 78·5° C., and are thought to be mainly lignoceric acid. E. B. D.

Polarographic Determination of Tin in Foods and Biological Materials. E. M. Godar and O. R. Alexander (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 681–684)—The method is accurate to about ±5 per cent. for concentrations of tin greater than 10 p.p.m., but is applicable to concentrations as low as 0·5 p.p.m. Much smaller samples than in the iodimetric method (A.O.A.C., *"Official and Tentative Methods of Analysis,"* 5th Ed., 1940, p. 413) are used. Since a mercury pool anode causes reduction of stannic tin, an external saturated calomel reference electrode is used. The design of the polarographic cell permits nitrogen to be passed either through or over the surface of the solution.

Method—Take 5 to 10 g. of sample, add 10 to 15 ml. of nitric acid and 2 to 3 ml. of sulphuric acid. Heat slowly, adding small amounts of nitric acid as charring occurs. When fumes of sulphur trioxide are evolved with no further darkening or charring, add 1 ml. of perchloric acid and continue heating until the latter has volatilised. Allow to cool, add 10 to 15 ml. of water, and transfer to a 50-ml. conical centrifuge tube, washing in with a little water and finally diluting to approximately 20 ml. Add 1 ml. of aluminium chloride solution (4·65 g. of the nonahydrate [? hexahydrate.—Ed.] in 250 ml. of water; 1 ml. ≡ 2 mg. of Al), and 1 drop of methyl red. Make alkaline with concentrated aqueous ammonia, adding 0·1 to 0·2 ml. in excess, but avoid a large excess. Centrifuge at high speed and decant the clear liquid as completely as possible. Add to the residue 2·5 ml. of hydrochloric acid (1+1) and shake to dissolve. Dilute to 10 ml. with saturated ammonium chloride solution. Transfer a 4- to 5-ml. portion to the cell and add 1 drop of saturated cresol red solution. Bubble nitrogen through the solution for 10 min., then divert the gas to blanket the surface. Record the polarogram between 0 and 0·8 v. at the highest sensitivity permitting the recording of the complete curve. Measure the height of the second tin wave and calculate the tin content of the sample from a calibration curve prepared as follows. Transfer aliquots of standard tin solution (dissolve 0·5 g. of tin in 250 ml. of hydrochloric acid and dilute to 500 ml.; dilute 25 ml. to 250 ml. with hydrochloric acid (1+1): 1 ml. = 0·1 mg. of Sn) to centrifuge tubes, dilute, and precipitate as described above. Record the polarograms, measure the wave heights, and plot the latter against the concentrations of tin. Run additional standards at intervals.

Iron, copper, bismuth, cadmium, mercury, antimony, nickel, cobalt, and zinc in equal or slightly greater concentrations do not interfere, but lead is precipitated with tin, and is reduced at a voltage too near to that of the second tin wave to be resolved. The interference is not serious in the analysis of foods, in which the lead concentration is relatively minor. When significant amounts of lead are suspected, proceed as follows. Record the polarogram as usual, and measure the combined wave height due to tin and lead. To a 5-ml. aliquot add 1 ml. of concentrated aqueous ammonia and 0·5 ml. of ammonium citrate solution (50 per cent. w/v). Record the polarogram and measure the height of the lead wave (tin is completely suppressed). Prepare tin-free solutions containing known amounts of lead, and precipitate in the presence of aluminium as above. Dissolve and take a polarogram in the supporting electrolyte of hydrochloric acid and ammonium chloride. Repeat after addition of ammoniacal citrate. Plot the lead wave heights in acid medium against those in alkaline medium. Use the curve to convert the height of the lead wave given by the sample in alkaline medium to the equivalent height in acid medium. Deduct this computed wave height from the combined wave height of tin and lead to obtain that due to tin.

J. T. S.

Biochemical

Simplified Method for the Determination of Sodium [in Biological Fluids]. J. T. Bradbury (*J. Lab. Clin. Med.*, 1946, **31**, 1257–1261)—In an investigation of the ability of various diuretics to cause excretion of sodium, it became necessary to develop a method for the rapid determination of that metal in urine. The uranyl zinc acetate procedure of Barber and Kolthoff (*J. Amer. Chem. Soc.*, 1928, **50**, 1625; 1929, **51**, 3233) as modified by Butler and Tuthill (*J. Biol. Chem.*, 1931, **93**, 171) and by Salit (*Ibid.*, 1932, **96**, 659) has been simplified by measuring the colour of the supernatant fluid after the precipitation of the triple acetate, the reduction in colour being found to be proportional to the amount of sodium present originally.

Procedure—Transfer 1 ml. of clarified urine, deproteinised serum, or other sodium-containing fluid, which might be expected to contain between 1 mg. and 10 mg. per ml. of the metal, to a 15-ml. centrifuge tube, add exactly 4 ml. of freshly filtered uranyl zinc acetate reagent and 2 ml. of 95 per cent. alcohol, and mix throughly. The reagent should be prepared according to the method of Weinbach (*Ibid.*, 1935, **110**, 95), or by dissolving 77 g. of uranyl acetate in a mixture of 800 ml. of water and 14 ml. of glacial acetic acid, adding 281 g. of zinc acetate in small quantities, then 7 ml. of glacial acetic acid together with sufficient water to produce nearly 1 litre and, finally, after leaving overnight, diluting to exactly 1 litre. If urine is being examined, a control solution should be prepared as above except that 4 ml. of water are substituted for the uranyl zinc acetate reagent. Centrifuge the mixture, decant the clear supernatant fluid into the absorption cell of a photo-electric colorimeter, and determine the intensity of the colour, using a blue filter with a Fisher electrophotometer; 3-ml. microcells are specified and a blue filter No. 425 is employed. Subtract the photometer reading of the blank from that of the test, and correlate the value found with the quantity of sodium by reference to a graph constructed from data obtained by submitting standard solutions of sodium chloride to the above procedure.

The method has been checked by comparison with results obtained gravimetrically; satisfactory agreement was obtained. The urine should be prepared for the test by allowing ammonia to bubble through the sample until it is strongly alkaline. It should be set aside in a refrigerator for several hours, and then filtered. Albumen may be removed,

if present, by adding mercuric chloride or trichloroacetic acid. Blood or serum may be deproteinised by mixing with an equal volume of 20 per cent. trichloroacetic acid, stirring vigorously, and removing the precipitate by centrifuging. J. A.

Estimation of Cobalt in Biological Materials with Nitrosocresol. G. H. Ellis and J. F. Thompson (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 254–257)—*o*-Nitrosophenol forms coloured complex compounds with many metals, but only those of ferric iron, palladium, and cobaltous cobalt are soluble in light petroleum. With most plant and animal tissues only the interference due to iron must be eliminated in order to give a colorimetric cobalt determination. Where the cobalt content is very small relative to the iron, interference is not completely avoided by use of a citrate buffer, but separation can be achieved by using sodium diethyldithiocarbamate or, more generally, dithizone. *o*-Nitrosocresol is preferable in that it is more easily prepared than *o*-nitrosophenol and produces a more intense colour with cobalt. The method described is suitable for use with 1 to 10 g. of dry animal or plant tissue containing 0·02 to 25 μg. of cobalt.

REAGENTS—(1) *Stock cupric o-nitrosocresol solution*—Dissolve 6 g. of hydroxylamine hydrochloride and 15 g. of cupric chloride in 900 ml. of water, and add 5 ml. of *m*-cresol. Stir in 15 ml. of 30 per cent. hydrogen peroxide. After 2 hr., add 25 ml. of concentrated hydrochloric acid and extract the reagent with successive portions of light petroleum. Wash the extract with water and 50- to 100-ml. portions of 1 per cent. aqueous cupric acetate until the upper layer is colourless. The deep-red, aqueous solution of the cupric complex is then stored in a refrigerator; it is stable for months.

(2) *Sodium borate buffer*—Dissolve 20 g. of boric acid in 1 litre of water and add 22·8 ml. of 1·0 *N* sodium hydroxide to give *p*H 7·7 to 7·8.

(3) *Sodium nitrosocresol solution*—Add 10 ml. of concentrated hydrochloric acid to 75 ml. of the stock copper-complex solution and shake with 300 to 500 ml. of light petroleum. Wash this phase with two 100-ml. portions of 0·01 *N* hydrochloric acid and two 100-ml. portions of re-distilled water. Add 25 ml. of a borate buffer made by diluting 1 litre of the borate solution, prepared as above, with 20 ml. of *N* sodium hydroxide solution, and shake. Remove the buffer solution and repeat this treatment until the light petroleum layer is almost colourless; stored in a refrigerator the aqueous reagent is stable for about a month.

(4) *Carbamate solution*—Shake a 0·1 per cent. aqueous solution of sodium diethyldithiocarbamate with carbon tetrachloride to remove copper and cobalt.

(5) *Dithizone solution*—Dissolve 0·5 g. of dithizone in 600 to 700 ml. of carbon tetrachloride and filter into 2·5 to 3 litres of 0·02 *N* aqueous ammonia and shake; discard the non-aqueous layer. Shake then with 50-ml. portions of carbon tetrachloride until a pure green layer settles after standing. Add 1 litre of the tetrachloride and acidify slightly with hydrochloric acid; shake well, separate, and store the solution in a cool, dark place.

(6) *Hydroxylamine-acetate buffer*—Dissolve 10 g. of hydroxylamine hydrochloride and 9·5 g. of sodium acetate (anhydrous) in 500 ml. of re-distilled water; the *p*H of the solution should be 5·0 to 5·2.

(7) *Potassium nitrate solution*—Shake a 5 per cent. solution of potassium nitrate with 0·1 per cent. aqueous carbamate solution and carbon tetrachloride.

(8) 40 *per cent. ammonium citrate solution*—Dissolve 800 g. of citric acid in 600 ml. of water and add slowly 900 ml. of concentrated aqueous ammonia. Adjust to *p*H 8·5, if necessary. Dilute to 2 litres and extract with 10-ml. portions of dithizone in carbon tetrachloride until the aqueous phase remains orange-coloured. Then extract with tetrachloride until the orange colour is removed.

(9) *Ligroin* [*light petroleum*], *b.p.* 70 *to* 90° C.—Distil over dilute alkaline permanganate and wash by vigorous shaking with water.

(10) *Standard cobalt solution*—Dry cobalt sulphate heptahydrate at 250 to 300° C. for 6 to 8 hr., and dissolve 0·263 g. in 50 ml. of re-distilled water, and 1 ml. of sulphuric acid. Dilute to 1 litre, and dilute further as required.

(11) *Ammonia solution*—Distil concentrated aqueous ammonia into an equal volume of re-distilled water.

(12) *Phenolphthalein*—A 1 per cent. solution in 95 per cent. ethanol.

(13) *Bromothymol blue*—A 0·04 per cent. aqueous solution of the sodium salt.

Reagent grade perchloric acid (60 or 72 per cent.), redistilled hydrochloric acid (1+1), and nitric acid (1+1) are also required. Also distil carbon tetrachloride over lime and filter through acid-washed paper. All distillations must be done in Pyrex apparatus.

METHOD. *Preparation of sample*—Tissues may be ashed by the usual methods, nitric acid and potassium nitrate being used, if necessary. High silica contents should be removed with hydrofluoric acid and perchloric acid; otherwise adsorption is reduced by heating the ash solution for several hours before neutralising.

Separation of cobalt from iron. Dithizone extraction—Add 1 ml. of ammonium citrate for each gram of dry tissue used and adjust the *p*H to 8·5 by means of aqueous ammonia (phenolphthalein). Shake for 30 sec. with 10 ml. of dithizone solution, repeating the extraction if necessary, so that the green coloration is unchanged. Evaporate the extracts to dryness. *Carbamate extraction*—Proceed

as above, but adjust the *p*H to 6·5 (bromothymol blue). Add dropwise with shaking 5 ml. of the 0·1 per cent. solution of the reagent and 10 to 20 ml. of tetrachloride, and shake vigorously for 10 min. Evaporate this extract, which also contains any copper present, to dryness.

Determination of cobalt—Oxidise the residue obtained from either extraction with 2 ml. of perchloric acid in a covered beaker. When the solution is colourless, remove the perchloric acid, and add 5 ml. of 0·01 *N* hydrochloric acid and 5 ml. of the borate buffer solution. Transfer to a 60-ml. separating funnel and add sodium nitrosocresol solution dropwise until reaction with the copper is complete, as shown by the appearance of an orange colour. Add 1 ml. of the reagent in excess, then 4 to 5 ml. of ligroin and shake for 5 min. Remove the aqueous phase, and to the ligroin add 5 ml. of 1 per cent. aqueous cupric acetate solution. Shake for 1 min. and again separate; wash the ligroin layer with water and finally with 5 ml. of the hydroxylamine-acetate buffer. Unless much cobalt is present the solution is colourless, absorption occurring in the near ultra-violet. Transfer to a 5- or 10-cm. absorption tube and read in a photo-electric colorimeter using a light band near 360 mμ, where maximum absorption occurs.

Blank determinations should be carried out, especially where conditions require a large deviation from the usual procedure, using either the blank, or pure ligroin as the reference liquid. Since Beer's law holds over a wide concentration range, calibration is relatively simple. In a 10-cm. tube, 0·01 μg. of cobalt per ml. transmits about 90 per cent. of incident light in the recommended wave-band.

Results—With cobalt contents of about 0·03 μg. the range of recovery is from 96 to 107 per cent., and with contents of about 0·2 μg., from 89·0 to 104·5 per cent. An average on 20 determinations is 97·4 per cent. with determinations in both ranges. The values agree well with those obtained by the nitroso-R-salt method.

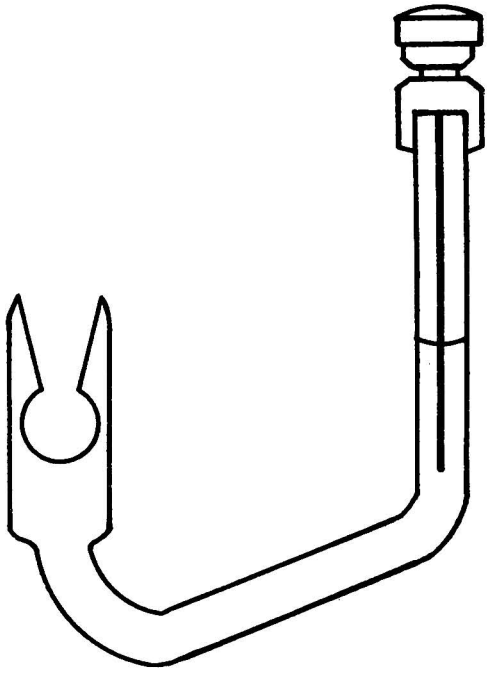
Discussion—Cobalt nitrosocresol is determined in a smaller volume of solution and the test is therefore more sensitive than that with the nitroso-R-salt. Ashing at 650° C. prevents adsorption of copper and iron on the silica vessel and the results for cobalt are not affected unless the vessel is badly etched. The use of the hydroxylamine-acetate buffer causes the ferric complex to be reduced to a form soluble in the aqueous phase, but is not effective in presence of more than a ten-fold excess of iron. Dithizone removes all ferrous iron and is widely applicable, whilst carbamate is useful in that it reacts at a lower *p*H and thus is less likely to precipitate any salts present; also, a single extraction is often sufficient. Copper can be determined in the same extract since the cobalt to copper ratio is usually small, and the copper coloration is not altered. Copper may also be determined after removal of the aqueous phase from the ligroin solution of the cobalt-complex, either directly or after first evaporating the solution to dryness with 1 ml. of perchloric acid. M. E. D.

Organic

System of Characterisation of Pure Hydrocarbons. Refractometric Analysis as a Key to the Evaluation of Structure. R. T. Wendland (*J. Chem. Educ.*, 1946, **23**, 3–15)—A system for the classification of hydrocarbons according to several of their physical properties, and according to their response to a few simple chemical tests, is the basis of a method for determining the nature of these compounds. The properties required are boiling point, density, refractive index, specific dispersion, and specific refraction. By comparison of the properties of an unknown hydrocarbon with the chemical properties and the limiting values of the physical properties recorded in the various classes, divisions, and groups of the table given in the paper, the compound can be shown to be a member of one particular sub-group. To identify the compound, it is then necessary to distinguish it from a small number of closely related compounds. A further comparison of properties and, when possible, the preparation of derivatives, will usually provide strong evidence in favour of one of the possible structures. In order to exemplify the working of the new scheme of classification, various hydrocarbons chosen at random from the literature were correctly placed in the sub-groups having properties corresponding to their properties, the structure of each hydrocarbon chosen being included in the structures listed in the sub-group of the classification. B. A.

Micro-titration of Organic Acids. W. Ingold (*Helv. Chim. Acta*, 1946, **29**, 1929–1936)—A potentiometric method is used. The re-entrant glass electrode shown also acts as titration vessel; the bulb has a capacity of about 1·5 ml. A suction pipette, the tip of which is plugged with cotton wool, enables the vessel to be emptied without danger of puncturing the glass membrane. The calomel reference electrode has a fine, hooked outlet which may be flushed out with potassium chloride solution by the operation of a tap. The microburette is of horizontal, tapless form (*cf.* Hybbinette and Benedetti-Pichler, *Mikrochem.*, 1942, **30**, 15) with a paraffined jet, has a capacity of about 0·15 ml., and can be read to 0·0001 ml. It is filled by suction and has a soda-asbestos guard tube to prevent ingress of carbon dioxide. A lever mechanism enables the burette tip to be immersed in the test solution for delivering. Potassium hydroxide and tetramethylammonium hydroxide solutions (not less than 0·1 *N* and free from carbonate) are preferred as titrants, since the alkali error of the glass

electrode is less than with sodium or lithium hydroxides. The test solution is stirred by a stream of carbon-dioxide-free nitrogen.



Before introducing the sample, rinse the titration vessel and dry the conical neck, first with a cotton plug and then with chamois leather. Add the sample (300 to 900 μg.); boiled-out distilled water or alcohol-water mixtures are the usual solvents. The bulb of the vessel should be not more than two-thirds full. Arrange the tips of the reference electrode and gas inlet tube to dip into the solution, and stir by passing 2 to 3 bubbles per sec. Clamp the micro-burette so that operation of the lever immerses the burette tip 1 to 2 mm. in the solution, connect to a suitable *p*H meter, and titrate. The error is ±5 per cent. with organic acids of molecular weight 100 to 500. J. T. S.

Conversion of Organic Sulphur to Hydrogen Sulphide for Analysis. E. Field and C. S. Oldach (*Ind. Eng. Chem., Anal. Ed.*, **1946**, **18**, 668–669)—Since many catalytic processes are affected by traces of hydrogen sulphide or organic sulphur, sensitive analytical methods are necessary to determine and eliminate them. Satisfactory methods of determining hydrogen sulphide are available, *e.g.*, the Field and Oldach colorimetric method (*Ibid.*, 1946, **18**, 665) also the Moses and Jilk lead-acetate-impregnated tape method (U.S. Patent 2,232,622, Feb. 18th, 1941). The following technique involves the conversion of volatile organic sulphur compounds to hydrogen sulphide, which may then be determined by any suitably accurate method. Jilk's procedure (*Proc. Amer. Soc. Testing Materials, Preprint* 89, 1939) has been modified by raising the reaction temperature to 900° C., thus rendering moistening of the gases unnecessary, and also allowing an oxygen content of up to 1 per cent. without affecting the results.

Procedure for gases—Pass the gas with an excess of hydrogen over 6 ml. of 14- to 20-mesh alumina in a 10 mm. I.D. quartz tube heated to 900° C. All connecting lines must be of glass and, where they are unavoidable, rubber joints must first be boiled with sodium hydroxide to remove sulphur. Maintain a gas rate not exceeding 0·6 litre per min. Taking precautions to reduce errors due to adsorption, absorb the emerging gases in 6 per cent. sodium hydroxide solution in a Milligan bubbler.

Procedure for liquids—Pass sulphur-free hydrogen at the rate of 0·6 litre per min. through the liquid sample contained in a warmed bubbler, adjusting the volume and temperature of the sample to give a convenient sulphur content and rate of evaporation. Pass the gases then over heated alumina as before, absorbing the emergent gases in sodium hydroxide, until the weighed sample is completely volatilised. Take the same precautions against adsorption as with gaseous samples. With high-boiling liquids, it is necessary only to strip off the low-boiling sulphur constituents. Deposition of carbon on the catalyst lowers its activity and increases adsorption; hence the catalyst must be regenerated by passing air over it at 900° C. for 5 min., and purging with hydrogen before each regeneration. If this is effected during an analysis, the air must be by-passed round the absorbing solution to prevent oxidation of the sulphide.

Demonstration of conversion to hydrogen sulphide—Using 14- to 20-mesh alumina at 900° C., and a carrier gas of pure hydrogen or water gas and introducing a measured volume of vapour into the stream, hydrogenation was demonstrated for carbonyl sulphide, carbon disulphide, methyl mercaptan, methyl isocyanate, thiophen, and sulphur dioxide. Errors of up to ±4 per cent. on pure compounds were attributed to experimental inaccuracies.

Adsorption of sulphur on catalyst—With a fairly uniform gas sample, adsorption errors are reduced by allowing the catalyst to come to equilibrium with the gas before starting an analysis. With batch samples and liquids, the catalyst must be purged with pure hydrogen before and after treating the sample, 28 litres being necessary to remove all the sulphur from 6 ml. of 8- to 14-mesh alumina at 900° C.

The method is widely applicable, and traces of sulphur have been determined in hydrogen, carbon monoxide, methane, ethylene, nitrogen, and coke-oven gas; methanol, benzene, *cyclo*hexane, tetralin, and white oil. The presence of water-vapour is not essential, but it often reduces carbon deposition.

Carbon dioxide does not interfere unless in sufficient quantity to deteriorate the absorbing solution. Unsaturated compounds are not deleterious. Oils and tars forming in the scrubber may affect results, but any absorbed hydrogen sulphide can then be liberated by acidification and again absorbed in alkali. M. E. D.

Inorganic

Method of Semi-Quantitative Inorganic Analysis. P. E. Wenger, D. Monnier, and A. Piguet (*Helv. Chim. Acta*, 1946, **29**, 1698–1701)—On the basis of the tests recommended in the second Report of the International Commission (of the Union Internationale de Chimie) on new analytical reagents and reactions, it should be possible to establish a series of rapid semi-quantitative tests for each element. It is intended to examine this possibility element by element. This is a preliminary report, in which details are given of an estimation of copper based on the limit of perceptibility of the test given by copper with several reagents. Reagents chosen for this purpose must be sufficiently selective, and have as great a difference of sensitivity as possible. Tables are prepared that give directly, from the limit of perceptibility, the percentage of the element in the sample being examined.

Reagents—A 1 per cent. solution of rubeanic acid in 96 per cent. alcohol, a 0·1 per cent. solution of sodium diethyldithiocarbamate in water, a 1 per cent. solution of potassium ethylxanthate in water, and a 1 per cent. solution of benzoinoxime in alcohol. Carry out the tests on filter papers impregnated with the reagent and dried.

Method—Prepare solutions containing, A, 0·1 g.; B, 0·004 g.; and C, 0·002 g. of copper per litre. On a spot plate place 1 drop of A and 9 drops of water to give A_1, 2 drops of A and 8 drops of water to give A_2, and so on to . . . . 10 drops of A to give A_{10}. Similarly, prepare B_1 to B_{10} and C_1 to C_{10}. Determine which are the most dilute solutions that give perceptible tests with the test papers of the four reagents. To estimate the copper in a substance, take exactly 0·1 g. of sample, dissolve it in the minimum quantity of a suitable solvent, and dilute to 1 litre to obtain solution A^e. Prepare from this solution A^e_1 to A^e_{10}, B^e_1 to B^e_{10}, C^e_1 to C^e_{10}. Find the limits of perceptibility as before. Prepare a table showing the percentage of copper corresponding to the possible positions of the limit for each reagent. For rubeanic acid, the limit found by using the standard solutions is C_3, and if the limit in the estimation is C^e_3 the sample is 100 per cent. copper; if it is C^e_4, 75 per cent. copper; and if A^e_1, 6 per cent. of copper. From the table and the limit found, deduce the amount of copper in the sample.

For a copper content of 2 to 10 per cent. the result is accurate to ±1 per cent., and for higher contents to ±5 per cent. Two examples are given of the application of the method to the estimation of copper in alloys. If the sample dissolves without great difficulty, the estimation can be completed in 30 min. B. A.

Sensitivity of Precipitation Reactions in Dilute Electrolytes. R. K. McAlpine (*J. Chem. Educ.*, 1946, **23**, 28–34)—Factors considered in this discussion of the sensitivity of the lead chloride, lead iodide, and lead chromate precipitation tests for lead are solubility, the common ion effect, supersaturation, and visibility of the precipitate.

When the sensitivities of the tests for lead, in which lead chloride or lead iodide is precipitated from aqueous solutions, are examined, it is found that both tests are less sensitive than is indicated by calculations based on the solubility product principle. The discrepancies are not due to the formation of supersaturated solutions, nor to inability to observe the precipitate, but are caused partly by inter-ionic attraction and partly by the formation of ions such as $PbCl^+$ and PbI^+. It is probable that the reduced sensitivity of the lead iodide test in the presence of perchloric acid is the result of inter-ionic attraction, whilst the reduced sensitivity of the same test in the presence of chloride ions is due to the formation of $PbCl^+$. From measurements now made of the sensitivity of the lead chloride and lead iodide tests in the presence of an excess of potassium chloride and potassium iodide, respectively, and known data on the solubilities of the lead salts in water, assuming that lead chloride and lead iodide are completely ionised in aqueous solution, the apparent values of the dissociation constants of the ions $PbCl^+$ and PbI^+ can be calculated. The value for the constant for $PbCl^+$ appears to lie between 0·05 and 0·01, and that for PbI^+ between 0·005 and 0·001. However, observations made on the precipitation of lead iodide by an excess of lead perchlorate indicate a value between 0·05 and 0·01 for the dissociation constant of PbI^+. When an excess of potassium iodide is used for the precipitation of lead iodide, the formation of complex ions such as $PbI_4^{''}$ may have a significant effect on the solubility of the lead iodide. If the reagent in excess is lead perchlorate, the possibility of the formation of ions other than those considered in the calculations is less, and therefore the second value for the dissociation constant of PbI^+ is probably the more correct. Because of small effects due to supersaturation and inter-ionic attraction, this value will be slightly low. The marked reduction in the sensitivity of the lead iodide precipitation test that occurs when nitrate ion is added, can be explained by the existence of the ion $PbNO_3^+$ with a dissociation constant greater than that of $PbCl^+$.

The solubility of lead chromate, in the presence of excess chromate, is negligible compared with the amount of precipitate, 0·01 to 0·02 mg. of lead in 50 ml. of solution, required to produce a recognisable opalescence. Calculations based on solubility product give the correct order of the sensitivity of the test when it is carried out in the presence of perchloric acid. B. A.

Colorimetric Determination of Fluoride. D. Monnier, Y. Rusconi, and P. Wenger (*Helv. Chim. Acta*, 1946, **29**, 521–525)—The soluble, violet-coloured sulpho-5-salicylic acid ferric complex is decolorised by fluorides because of the formation of the more stable FeF_6''' ion. As Beer's Law is not obeyed, calibration curves must be used, and they are prepared by adding known amounts of fluoride to a solution of the complex, and determining the extinction, E, in a Pulfrich photometer using a number 4 filter, and plotting K (E/length of tube in centimeters) against fluoride concentration. The ferric sulphosalicylate complex is stable in an excess of the acid in the absence of fluoride. The fading is not solely dependent on the fluoride concentration, although this is the chief factor, and the colour tends to return. Reproducible results are obtained if sufficient sulphosalicylic acid is present to give the maximum intensity of coloration of the complex. This value was determined by investigating the composition of the complex, which was found to contain one molecule of the acid to one ferric ion as compared with the ferric salicylate complex which contains two molecules of salicylic acid to each ferric ion.

Calibration solutions—(A) 2 ml. of 0·11 per cent. ferric chloride solution, 0·8 ml. of *N* ammonium chloride, 2 *N* hydrochloric acid to *p*H 3, and 0·75 ml. of 0·5 per cent. sulphosalicylic acid solution, the mixture being diluted to 20 ml.

(B) 5 ml. of 0·11 per cent. ferric chloride solution, 2 ml. of *N* ammonium chloride, 2 *N* hydrochloric acid to *p*H 3, 1·9 ml. of 0·5 per cent. sulphosalicylic acid solution, diluted to 25 ml.

(C) 10 ml. of 0·11 per cent. ferric chloride solution, 2 ml. of *N* ammonium chloride, 2 *N* hydrochloric acid to *p*H 3, and 4 ml. of 0·5 per cent. sulphosalicylic acid solution, diluted to 25 ml.

The calibration curves are prepared by adding known quantities of 0·2 per cent. sodium fluoride solution to these solutions and determining K, the sodium fluoride solution having been previously adjusted to *p*H 3 with a few drops of hydrochloric acid. As the fading action tends to decrease on keeping the solutions, the determinations should be made within 3 to 4 hr. The solutions are useful within the ranges; A—0·10 to 1·0 ml. of 0·2 per cent. sodium fluoride solution, B—0·25 to 3 ml. of the fluoride solution, and C—1·0 to 6·0 ml. of the fluoride solution.

Analyses show that the method is applicable to low fluoride contents; it gives a maximum error of 5 per cent.

Procedure—Take 5 ml. of 0·11 per cent. ferric chloride solution, 2 ml. of *N* ammonium chloride, and add hydrochloric acid to adjust the *p*H to 3. Add 1·9 ml. of 0·5 per cent. sulphosalicylic acid solution and a small volume of the fluoride solution to give a convenient fading. Dilute to 25 ml. Measure E, divide by the length of the tube in centimeters to obtain K, and refer to the abscissa of the appropriate calibration curve. The ordinate gives the fluoride content.

The effects of the presence of other ions, concentration changes, temperature, and dilution on the method are being investigated. M. E. D.

Constitution of Molybdenum Blue. W. D. Treadwell and Y. Schaeppi (*Helv. Chim. Acta*, 1946, **29**, 771–783)—Molybdenum blue, produced in the reduction of acid solutions of molybdates, is a combination of quinque- and sexavalent molybdenum oxides. The molecular proportions of these oxides vary with the method of preparation. As a large change in this ratio causes only a slight difference in percentage composition, composition has been determined oxidimetrically and conductometrically. *Oxidimetric method*—Electrically produced molybdenum blue hydrated oxide, precipitated in dilute sulphuric acid, was titrated in sulphuric acid solution by potassium permanganate to determine the quinquevalent molybdenum. The molybdenum of the titrated solution was reduced to the tervalent stage in a cadmium reductor, and the titration with permanganate repeated to determine the total molybdenum. The ratio of the two amounts of permanganate used clearly indicated the proportions of quinque- and sexavalent oxides, which were found to be $Mo_2O_5.4MoO_3$. *Conductometric method*—A solution of 500 mg. per litre of the electrolytic molybdenum blue was titrated conductometrically with 0·1 *N* sodium hydroxide, 100 ml. of the solution being used. For comparison, 100 ml. each of saturated molybdenum solution and 0·001 *N* sulphuric acid were similarly titrated. The acidity of the molybdenum blue was approximately that of molybdic acid. No appreciable amount of sulphuric acid was detected in the precipitate, and the acidity was attributed not to adhering sulphuric acid, but to acid hydroxyl groups. The results of these titrations, together with the molecular weight of 436 determined by the freezing point method, indicated that the aqueous solution of molybdenum blue hydrated oxide contained 1 hydrogen ion per $\frac{1}{2}$ $Mo_2O_5.2MoO_3$. A structural formula that explains the deep colour and the tendency to form negative sols, is proposed.

In sulphuric acid solution, molybdenum blue forms complex compounds with phosphoric and

arsenic acids, as well as with sulphuric acid. Solutions of molybdenum trioxide in sulphuric acid and the same solution of molybdenum reduced to the tervalent state were mixed to give solutions containing molybdenum of mean valency 5, 5·1, 5·2 . . 6, the total concentration of molybdenum remaining constant. Colorimetric determinations showed the colour to be strongest if the mean molybdenum valency was 5·67 (curves are given). Phosphates were prepared from the above sulphates as follows: a series of the solutions, containing the same total amount of molybdenum, were placed in 50-ml. flasks, diluted with a known amount of water until decolorised, the same amounts of phosphate solution being added to all, and the mixtures were made up to the mark. They were then kept for 1 hr. in boiling water, and the blue colour was determined colorimetrically after (*a*) 24 hr., or (*b*) 50 hr. In the first tests, the molybdenum blue was in large excess; in others, the amount of phosphate was increased. Molybdenum blue arsenates were similarly prepared. The 24-hr. curves showed that the reduction proceeded by stages; the 50-hr. curves were smooth. The first tests on sulphate, phosphate, and arsenate all showed maximum colour strength when the mean molybdenum valency is 5·67, but with increasing amounts of phosphoric or arsenic acid the valency for maximum colour decreased; this was due to the formation of Mo^{V} phosphate or arsenate in a side reaction. For a given amount of molybdenum sulphate of optimum valency, increasing amounts of phosphoric acid increased the blue colour until the ratio $1PO_4$:12Mo was reached. Pyrophosphate is similar to phosphate in the development of molybdenum blue, giving the same result. Sodium hypophosphate, $Na_2H_2P_2O_6$, in sulphuric acid solution gave a violet-blue colour very quickly in the cold; under the same conditions, the hypophosphate colour was much more intense than that of the phosphate. A molybdenum blue perchlorate could not be prepared. E. B. D.

Separation of Calcium from Magnesium by the Oxalate Method in Samples of High Magnesium - Calcium Ratio. E. R. Wright and R. H. Delaune (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 426–429)—The procedure in which a large amount of oxalate is employed to prevent the precipitation of magnesium oxalate and to ensure maximum precipitation of calcium has been investigated. Solubility data are given for calcium oxalate and magnesium oxalate in hot ammonium oxalate solutions of a range of concentrations. As the oxalate concentration is increased, the solubility of magnesium oxalate increases considerably, presumably owing to the formation of a complex ion. Three modes of precipitation have been examined. (A) Add 6 *N* aqueous ammonia dropwise to an acid solution at 70° to 80° C. containing 1·5 g. or more of ammonium oxalate monohydrate per 100 ml. until the liquid is alkaline to methyl red. Set aside for 1 hour without heating, and filter cold. When more than 5 g. of ammonium oxalate monohydrate are used, maintain the solution at 70° C. to prevent crystallisation of the reagent on cooling. (B) Add the sample solution dropwise to a hot ammonium oxalate solution of such a dilution that the final volume is 100 ml. Keep at 70° C. for 0·5 hr., and filter hot. (C) Heat 100 ml. of neutral sample solution containing approximately 1 g. of ammonium chloride to 80° C., add the amount of solid ammonium oxalate indicated in the table, stir until solution is complete, heat for 0·5 hr. at 80° C., and filter hot through a tared, fine porosity, glass filter crucible. Wash the precipitate with cold, 0·2 per cent. ammonium oxalate solution.

Method (A) gives more co-precipitation of magnesium than (B) or (C), but less precipitation of magnesium oxalate when insufficient ammonium oxalate is used. Method (B) is less convenient than (C), which gives almost equally good results. Methods (B) and (C) both give negligible co-precipitation of magnesium, but the result must be corrected for the solubility of calcium oxalate in the hot medium (see Table). Results of acceptable accuracy are obtained with magnesium - calcium ratios by weight up to 20:1 either by a single precipitation with method (C), using the correction factor; or by method (A) with not more than 5 g. of ammonium oxalate monohydrate and 0·2 g. of magnesium ion per 100 ml., a second precipitation of the calcium, cold filtration, and consequently no solubility correction.

RECOMMENDED QUANTITY OF AMMONIUM OXALATE

Magnesium present (g./100 ml.)	$(NH_4)_2C_2O_4.2H_2O$ (g./100 ml.)	Solubility correction (mg. of Ca/ 100 ml.)
0·10	7	0·20
0·20	11	0·35
0·30	15	0·60
0·40	20	1·4
0·50	25	2·0

The determinations are completed either by ignition of the precipitate to calcium carbonate at 475 to 500° C., or by permanganate titration.

L. A. D.

Solubility of Magnesium Ammonium Phosphate Hexahydrate. R. F. Uncles and G. B. L. Smith (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 699–702)—A systematic investigation of the solubility of magnesium ammonium phosphate hexahydrate in a range of salt solutions is reported. Added salts generally cause a considerable increase in solubility, ammonium salts having a greater effect than equivalent amounts of sodium or potassium salts. Molybdate and oxalate ions have a

very great effect, probably by the formation of complex ions. Calcium and barium ions also show exceptional behaviour by increasing solubility. Relatively small quantities of aqueous ammonia reduce the solubility of the compound in every salt solution examined, and with increasing additions of aqueous ammonia the solubility becomes negligible. The solutions commonly employed in the gravimetric determination of magnesium as phosphate by Epperson's method (*J. Amer. Chem. Soc.*, 1928, **50**, 321; ANALYST, 1928, **53**, 239) are such that the solubility is insignificant. The amount of dissolved magnesium was determined by the titan yellow absorptiometric method. The use of hydroxylamine hydrochloride, as suggested by Gillam (*Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 499), to reduce the rate of fading of the colour, has been found effective.

L. A. D.

Analysis of External Deposits from Boilers. Part I. General Remarks on the Nature of Boiler Deposits and their Examination. H. E. Crossley and A. H. Edwards (*J. Soc. Chem. Ind.*, 1946, **65**, 251–254). **Part II. Method for the Analysis of Deposits Rich in Phosphates. A. H. Edwards** (*Ibid.*, 254–256). **Part III. Method for the Analysis of the Water - Soluble Fraction of the Deposits. A. H. Edwards and D. Flint** (*Ibid.*, 256–257)—The methods described are those used by the British Coal Utilisation Research Association.

Part I—(*a*) *Collection of sample*—Record all relevant details of the samples; *e.g.*, position in the boiler, boiler operation conditions, whether the sample is from exposed or sheltered parts, the proximity to soot-blowers, local gas velocities, the nature of the fuel, etc. Note also the general character of the deposit *in situ*. (*b*) *Nature of the deposits*—The term comprises deposits found on all external surfaces of the boiler from the combustion chamber to the chimney, and the samples are conveniently divided into two groups. *Fly-ash material* consists of solid matter carried mechanically from the fuel bed, and is largely composed of fused or sintered coal ash, although in some parts of the boiler coke or oxidised coal may be present. The amounts of ferric oxide, alumina, titania, lime, magnesia, sodium and potassium oxides, silica, sulphur trioxide, and phosphorus pentoxide total at least 99 per cent., and the sum of the sodium and potassium oxides and phosphorus pentoxide is less than 7 per cent. The *secondary deposit* consists of condensed substances mixed with some fly-ash.. The condensed substances usually consist mainly of sulphates and sometimes phosphates of sodium, potassium, iron, and aluminium, together with free silica. There may be present more than 0·5 per cent. each of many elements occurring as traces in the fuel, *e.g.*, boron, copper, mercury, zinc, lead, tin, germanium, gallium, and possibly arsenic. Coal, coke, free acids, and moisture may also be present. Some of the effects of the composition of the sample on the course of the analysis are discussed.

Part II—PROCEDURE—Ignite 2·5 g. of the sample at 800° C. in a stream of pure oxygen, and determine the moisture by absorption in anhydrone, the carbon dioxide by absorption in soda-asbestos, and the sulphur trioxide by absorption on silver gauze at 800° C. Weigh the silver, wash with boiling distilled water, dry by means of alcohol and ether, ignite to dull redness, and reweigh to determine the loss of silver sulphate.

Grind the ignited original material and digest 1 g. with 6 ml. of concentrated hydrochloric acid. Dilute with 20 ml. of hot water, filter, burn the paper, fuse the residue with 3 g. of sodium carbonate, dissolve the fused mass in 10 ml. of concentrated hydrochloric acid and 2 to 3 ml. of 20-volume hydrogen peroxide, and add to the acid extract. Evaporate to dryness, and bake at 115° C. for 2 hr., extract with 5 ml. of concentrated hydrochloric acid and 50 ml. of water and filter off the silica, repeating the evaporation and baking as usual. Ignite the precipitate, treat with hydrofluoric acid, fuse the residue with 0·5 g. of sodium carbonate, add the hydrochloric acid solution of the fused mass to the main filtrate, and dilute the whole to 500 ml.

Sulphate—Dilute 100 ml. of the solution to 300 ml., add 1 ml. of concentrated hydrochloric acid, and 5 ml. of bromine water, and boil to remove excess of bromine. Precipitate barium sulphate by the usual method.

Phosphate—If less than 6 per cent. is present, use the method described in Part III. Otherwise, dilute 100 ml. of the silica-free solution to 250 ml., and add 10 ml. of concentrated nitric acid and 5 g. of ammonium nitrate. Warm to 75° C. and add 100 ml. of ammonium molybdate reagent heated to 40° C. Leave for 0·5 hr. at 50° C., and overnight at room temperature. Filter, leaving most of the precipitate in the beaker, and wash the precipitate and paper with 5 per cent. ammonium nitrate solution. Dissolve the precipitate in ammonia solution (1+2), and wash the paper thoroughly with water, keeping the total volume of solution below 200 ml. Add hydrochloric acid until a precipitate appears, and clear the solution by means of 2 or 3 drops of diluted ammonia solution (1+1). Add 50 ml. of magnesia mixture, heat nearly to the boiling point, add phenolphthalein and then dilute ammonia solution until the liquid is pink. Cool, add one-fifth of the solution's volume of concentrated ammonia solution and leave for at least 4 hr. Filter, and wash with diluted ammonia solution (1+20). Dissolve the precipitate in hydrochloric acid and reprecipitate.

Ignite the precipitate finally at 1000 to 1050° C. and weigh as $Mg_2P_2O_7$.

(*Reagents—Ammonium molybdate*—Dissolve 100 g. of pure molybdic acid in 80 ml. of concentrated ammonia solution and 400 ml. of water. Pour the solution slowly into a mixture of 40 ml. of concentrated nitric acid and 600 ml. of water, the mixture being continuously rotated during the process. Add a solution of 5 mg. of sodium ammonium phosphate crystals, heat the mixture to 65° C., shake frequently, and allow to cool overnight. Filter into a dark bottle. Do not keep for more than 2 months.

Magnesia mixture—Dissolve 55 g. of magnesium chloride, $MgCl_2.6H_2O$, and 105 g. of ammonium chloride in water, add a little hydrochloric acid, and dilute to 1 litre.)

Mixed oxides—To 250 ml. of the 500 ml. of solution from the silica removal add enough (usually 15 to 20 ml.) 0·2 *N* ferric iron solution (19·606 g. of ferrous ammonium sulphate dissolved in water and 10 ml. of concentrated sulphuric acid, oxidised by boiling with nitric acid, and diluted to 250 ml.) for precipitation of the phosphate. Add a few drops of nitric acid, heat nearly to boiling and neutralise (to methyl red or rosolic acid) with diluted ammonia solution (1+1). Boil, filter, and wash with cold, 5 per cent. ammonium nitrate solution. Dissolve the precipitate in 7 ml. of concentrated hydrochloric acid and reprecipitate. Filter, wash, ignite, and weigh. Dissolve the precipitate by fusing with 7 g. of potassium pyrosulphate and digesting the melt with dilute sulphuric acid. Evaporate to fuming, dilute, and filter to remove silica, which is recovered, ignited, weighed, and treated with hydrofluoric acid.

Iron—Dilute the solution to 250 ml. and take 100 ml. Oxidise with a few drops of 0·1 *N* potassium permanganate, add 3 ml. of 40 per cent. ammonium thiocyanate, and titrate with 0·05 *N* mercurous nitrate until the red colour disappears. Aluminium oxide plus titanium dioxide is calculated by correcting the weight of the original precipitate for its phosphoric acid and iron contents.

Calcium and magnesium are determined in the filtrate from the mixed oxides as oxalate (titration with potassium permanganate solution), and as magnesium ammonium phosphate, respectively. *Alkalis* are determined on a new portion of ignited material by the Lawrence Smith method.

Part III—*Preparation of water-soluble portion*—Weigh 2 g. of sample (−100 mesh) into a weighed, sintered-glass crucible (Pyrex SF. 2C4), and heat at 105° C. for 2 hr., and for periods of 1 hr. until consecutive weighings agree to within 0·05 per cent. Suspend the crucible by a fine wire in the neck of a 500-ml., round-bottomed bolthead flask, put 20 ml. of water in the crucible and 120 ml. in the flask, fit a reflux condenser, and boil the water in the flask for 2 hr. at such a rate that the crucible does not fill completely. Drain the filter by suction, wash with hot water, dry, and re-weigh. Dissolve any deposit of hydrolysed salts from the flask with two 2-ml. portions of hydrochloric acid and hot water. Keep the solution separate from the main extract. If the main solution contains suspended matter filter it off, dissolve in hydrochloric acid, and add it to the acid washings of the flask. Dilute the clear filtrate to 500 ml. Determine the "mixed oxides" on the acid extract.

Acidity and chloride—Titrate 50 ml. with 0·04 *N* sodium hydroxide to the end-points of methyl red and phenolphthalein. Determine chloride by Volhard's method in the titrated solution.

Sulphate and alkalis—Dilute 200 ml. to 500 ml., add 1 ml. of concentrated hydrochloric acid and 5 ml. of bromine water and boil out excess of bromine. Precipitate the sulphate by adding barium chloride solution, filter, ignite, and weigh. Evaporate the filtrate to 200 ml. and precipitate magnesium as hydroxide by adding a slight excess of barium hydroxide; filter, and wash. Add 20 ml. of freshly prepared, 10 per cent. ammonium carbonate solution to the boiling filtrate, filter, and wash with hot water. Dissolve the precipitate in hydrochloric acid and reprecipitate. Evaporate the combined filtrates to dryness, and heat the residue to 450° C. on a sand-bath to expel ammonium salts. Extract the residue with water, add 3 drops each of saturated ammonium oxalate solution and barium chloride solution, and leave for 4 hr. Add 1 ml. of concentrated ammonia solution and 1 ml. of ammonium carbonate solution, leave overnight, and filter into a weighed platinum dish. Add 0·5 ml. of hydrochloric acid, evaporate to dryness, heat the dish to 450° C., and weigh. Dissolve the mixed chlorides and determine sodium as sodium zinc uranyl acetate, and the potassium as perchlorate by means of perchloric acid and ethyl acetate.

Silicate—Determine by evaporating 200 ml. of solution to which 5 ml. of hydrochloric acid have been added, adding 5 ml. of sulphuric acid, evaporating to fuming, dissolving the salts in diluted hydrochloric acid, and filtering.

Mixed oxides—Determine as in Part II, omitting the addition of iron solution if the phosphorus pentoxide content of the original material is less than 6 per cent.

Iron, Calcium, and Magnesium—Determine as in Part II.

Phosphate—Take a portion of solution containing about 2 mg. of phosphorus, and use the phosphomolybdate method and volumetric finish of B.S. 1016, 1942. L. A. D.

Absorptiometric Determination of Silicon in Steels. C. H. R. Gentry and L. G. Sherrington (*J. Soc. Chem. Ind.*, 1946, **65**, 90–92)—A silicomolybdate complex is reduced to molybdenum blue by means of ferrous iron in presence of oxalic acid. When the sample contains tungsten, a hydrofluoric acid - nitric acid solution is used.

Method—Dissolve 0·25 g. of the sample by the most suitable of the following methods.

(*a*) Simmer with 70 ml. of 5 per cent. sulphuric acid until the sample is dissolved, boil for 5 min. with 30 ml. of 1·2 per cent. potassium permanganate solution, and add 20-volume hydrogen peroxide drop-wise until the hydrated manganese dioxide dissolves. Boil for 3 min., cool, and dilute accurately to 500 ml.

(*b*) Dissolve in 40 ml. of nitric acid (1+4), dilute to 150 ml., boil for 5 min., cool, and dilute accurately to 500 ml.

(*c*) Dissolve in 40 ml. of mixed acid (200 ml. of hydrochloric acid and 65 ml. of nitric acid diluted to 1 litre), dilute to 200 ml., boil for 5 min., cool, and dilute accurately to 500 ml.

(*d*) Add to the sample in a platinum dish 0·50 g. of ammonium fluoride and 12 ml. of nitric acid (1+2). Warm gently until solution is complete, add 1 g. of boric acid dissolved in 10 ml. of warm water, warm for 5 min., and transfer to a 500-ml. graduated flask. Add 12 ml. of nitric acid (1+2) and dilute to 500 ml. Allow to settle somewhat and filter about 100 ml. through a dry paper.

Pipette two 25-ml. portions (A and B) of solution into dry, 100-ml. conical flasks. Add to A 10 ml. of 2·5 per cent. ammonium molybdate solution, mix, and leave for 5 min. Add 10 ml. of 4 per cent. oxalic acid solution, mix, and add 5 ml. of 6 per cent. ferrous ammonium sulphate solution. Set the Spekker absorptiometer water-to-water 1·00 with 608 filters. Fill a 2-cm. cell with solution and take the drum reading. Add to B in order, mixing after each addition, 10 ml. of the oxalic acid solution, 10 ml. of the ammonium molybdate solution, and 5 ml. of the ferrous ammonium sulphate solution. Take the drum reading on this colour blank. The silicon content of the sample is determined from the difference of the readings. To determine a reagent blank, ferric iron must be present. The determination is therefore made on a solution with ferric sulphate added to correspond to the iron content of the sample, or on a standard steel sample of very low silicon content. In some samples, especially weld deposits, in which silicon occurs as silicate as well as silicide, methods (*a*), (*b*), and (*c*) lead to lower results than the hydrofluoric acid method (*d*), owing, presumably, to the insolubility of quartz and some of the silicates in the acid mixtures employed.

The use of oxalic acid prevents interference by phosphorus, arsenic, and vanadium. The reagent blank is chiefly attributable to silicon in the ammonium fluoride. L. A. D.

Determination of Copper in Cast Iron and Steels with Quinaldic Acid. J. F. Flagg and D. W. Vanas (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 436–438)—The application of the reagent to these analyses has been investigated and a satisfactory modification of the method of Zan'ko and Butenko (*Ber. Inst. physik. Chem., Akad. Wiss. Ukr. S.S.R.*, 1938, **9**, 99) evolved. It is somewhat long and no more accurate than other methods in general use. The advantages claimed are that the precipitate is of definite composition, the reagent is stable and water-soluble, and only simple apparatus is used. The reagent is prepared by the method of Hammick (*J. Chem. Soc.*, 1923, **123**, 2882), and is used as a 1 per cent. aqueous solution neutralised to *p*H 7 with sodium hydroxide.

Method—Dissolve 1·493 g. of sample in 15 to 20 ml. of *aqua regia*. Add 10 ml. of sulphuric acid (1+1) and evaporate to fuming. Dissolve the residue in 50 ml. of water and as much sulphuric acid (1+4) as is necessary. Filter on a Whatman No. 40 paper and wash the residue once with water, with 25 ml. of a solution of 10 g. of ammonium tartrate, and then once more with water. Add concentrated ammonia solution to the filtrate and washings until the liquid turns a deep cherry-red colour. Cool, adjust the *p*H to 3·0 ± 0·2 with dilute ammonia solution or with sulphuric acid. Heat to 70° to 80° C., add 5 ml. of quinaldic acid reagent for each milligram of copper, leave on a steam-bath for 0·5 hr., and then allow to cool. Collect the precipitate in a filter crucible and wash once or twice with cold water. Dissolve the precipitate in a few millilitres of hot hydrochloric acid (1+1), and rinse the crucible several times with the hot acid and then with water. Add 2 g. of tartaric acid and 2 ml. of quinaldic acid reagent to the solution and then add ammonia solution (1+4) until the *p*H is about 3. Heat and cool as before, filter on a weighed glass crucible, wash with cold water, dry at 115° to 120° C., and reweigh. One mg. of precipitate is equivalent to 0·01 per cent. of copper in the sample. A preliminary concentration of the copper by internal electrolysis may be employed instead of one precipitation, but this method gave a low result with an 18–8 steel. Dissolve 1 g. of sample in *aqua regia* in a tube about 38 mm. in diameter and 130 mm. long. Add 3 ml. of concentrated sulphuric acid and evaporate to fuming. Cool, add 10 ml. of water, boil, and add 1·2 g. of hydroxylamine hydrochloride in 10 ml. of water to reduce the iron. Add 2 ml. of hydrochloric acid (1+1) and 2 ml. of nitric acid (1+3) and immerse the connected electrodes, a platinum gauze cathode and an anode consisting of about 23 cm. of 99·99 per cent. aluminium wire bent into

a spiral or loop. Heat the contents of the cell to 70° to 80° C. until the deposition is complete (30 to 75 min.), remove the electrodes, running water over the cathode, and strip the deposit with concentrated nitric acid. Add 5 g. of ammonium acetate to the copper solution, adjust the *p*H to 3 to 3·5, precipitate the copper with 50 mg. of quinaldic acid, filter, wash, and dry as above.

L. A. D.

Determination of [Free] Acid in the Presence of Aluminium [Salts]. **R. P. Graham** (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 472–474)—The method suggested by T. J. I. Craig (*J. Soc. Chem. Ind.*, 1911, **30**, 184) and subsequently modified by W. W. Scott (Scott and Furman, "*Standard Methods of Chemical Analysis*," 1939, p. 16), [in which the free acid is titrated with standard alkali hydroxide to a phenolphthalein end-point, after addition of a neutralised solution of potassium fluoride to form with the aluminium salt the difficultly-soluble aluminofluoride, K_3AlF_6, and the potassium salt of the combined acid in the sample, but leaving the free acid unchanged], has now been further modified by delaying the addition of potassium fluoride until 99·5 per cent. of the neutralisation has been effected, instead of having it present before starting the titration.

It is shown that when this new modification is applied to solutions of known composition the low results given by the old technique are prevented, and that the higher results by the modified technique are in accordance with theory. The low results are ascribed to occlusion of free acid by the precipitated potassium aluminofluoride. A minimum molar ratio, $F'/Al^{\cdots}$, of not less than 6 is necessary in order to satisfy the stoicheiometrical requirements.

The titrations are carried out in paraffin-lined beakers and with solutions free from carbon dioxide. The point at which to add the potassium fluoride is found by means of pilot titrations. In the first of these, the fluoride is added at the beginning of the titration and the result assumed to represent 98 per cent. of the true titre. From this, the volume of standard solution corresponding to 99·5 per cent. neutralisation is calculated. This calculated volume of standard solution is then run in to a second trial titration before the fluoride is added. If the first volume of standard solution added in this second titration is then found to be less than 99·5 per cent. of that at the end-point, the volume added before the addition of the potassium fluoride is re-calculated, and the titration repeated.

The modified fluoride method has been applied to the determination of aluminium in neutral hydrated alumina.

Procedure—Weigh 0·23 g. of the sample and transfer to a 125-ml. conical flask. Add 50 ml. of standard 0·4 *N* sulphuric acid and boil gently, with additions of water to keep the volume constant, until solution is complete (2 to 3 hours). Concentrate to about 25 ml., cool, and titrate the excess of acid with standard alkali and phenolphthalein by the modified fluoride method, using 15 ml. of 2 *M* neutral potassium fluoride solution.

Tested against neutral, air-dried alumina, prepared by treating aluminium amalgam with distilled water, the volumetric method gave results in close agreement with those obtained by ignition to constant weight.

C. F. P.

Determination of Iron in the Presence of Cobalt. **E. A. Brown** (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 228–230)—The iron is separated from much of the cobalt by one ammonia precipitation. The thiocyanate colour is then assessed by means of an absorptiometer, the effect of the remaining cobalt being eliminated by the use of two colour filters. The method is suitable for determining 0·07 to 0·5 mg. of iron in the presence of up to 90 mg. of cobalt. An accuracy of ±3 per cent. is claimed. The colour is developed by adding 5 ml. of 10 per cent. ammonium thiocyanate solution to about 90 ml. of solution, containing up to 0·5 mg. of iron and 5 ml. of concentrated hydrochloric acid, and diluting to 100 ml. The absorptiometric readings are made without delay with filters having maximum transmission at 425 mμ and 525 mμ. An expression may be derived by which the iron content of the solution can be calculated from the two readings if it is assumed that the light absorption of the iron and cobalt components obeys Beer's Law and that the components behave independently of each other. The original paper should be consulted for the derivation of the expression, the determination of the constants in it, and a discussion of its range of usefulness.

L. A. D.

Entrainment of Cobalt and Sulphur in Iron Separations. **E. T. Pinkney, R. Dick, and R. S. Young** (*J. Amer. Chem. Soc.*, 1946, **68**, 1126–1128)—Separation of iron from cobalt and sulphate ions by sodium phosphate gives almost complete recovery of the cobalt (*cf.* North and Wells, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 859) and the sulphate in one precipitation. Separation of iron by aqueous ammonia in presence of ammonium salts gives almost complete recovery (98·9–99·6 per cent.) of sulphate in one precipitation, but cobalt is very strongly entrained in the ferric hydroxide precipitate. The amounts entrained vary widely even under standard conditions, and a large number of re-precipitations is necessary to complete the separation from ferric hydroxide in ammoniacal solution. Separation of iron by means of zinc oxide yields most of the cobalt and sulphate in one

precipitation if filtration is made in hot solution, although a second precipitation is required for accurate work, but if filtration is carried out in the cold, retention of cobalt is increased slightly and that of sulphate greatly. A table showing the effect of varying conditions in the zinc oxide precipitation gives lowest cobalt and sulphate recoveries when precipitation was in hot, and filtration in cold, solutions. Partial neutralisation of the acid with sodium carbonate before the addition of zinc oxide decreased recovery of both cobalt and sulphate. Large quantities of zinc oxide do not increase entrainment of these ions. E. B. D.

Determination of Uranium with 8-Hydroxyquinoline. A. Claassen and J. Visser (*Rec. Trav. Chim.*, 1946, **65**, 211–215)—The authors have obtained consistently low results when standardising uranium solutions by the method of Hecht and Reich-Rohrwig (*Monatsh.*, 1929, **53/54**, 596), in which the uranium is precipitated by 8-hydroxyquinoline. The method has been subjected to critical examination, and a modified procedure is now proposed.

The negative errors obtained are due partly to the high solubility (0·7 to 1·0 mg. of uranium per 100 ml.) of the precipitate, $UO_2(C_9H_6NO)_2.C_9H_7NO$, in the hot water used for washing. This error can be avoided by washing with hot, dilute oxine solution, in which the precipitate is practically insoluble. Small amounts of oxine adhering to the precipitate are expelled by heating at 110° C. The *p*H of the solution obtained by the procedure of Hecht and Reich-Rohrwig is poorly defined, the acidity often being high enough to prevent complete precipitation of the uranium. Precipitation is now found to be complete only in the range *p*H 5·0 to 9·0. Although Hecht and Reich-Rohrwig report that uranium oxinate remains constant in weight up to 170° C., it was found that 0·3719 g. of the compound, dried at 105° C., remained unchanged by further drying at temperatures up to 140° C., and then lost weight at 150° to 170° C., until at 180° C. decomposition set in. According to Fleck (ANALYST, 1937, **62**, 378), one molecule of oxine is lost by drying at 200° C., but weighing of the precipitate after heating at this temperature is not recommended as the time of heating is critical.

For use in the investigation, a known weight of standard uranium acetate solution containing about 200 mg. of uranium was made 1 to 2 *N* with respect to sulphuric acid and reduced in a cadmium reductor. Air was bubbled for five minutes through the solution, which was then titrated with standard potassium permanganate, *o*-phenanthroline-ferrous complex being used as indicator. As a check, other weights of the standard solution were heated to dryness in platinum with an excess of aqueous ammonia, and the residue ignited to U_3O_8.

Method—The proposed procedure for the oxinate precipitation is as follows: *Reagent*—Dissolve 4 g. of oxine in 8·5 ml. of concentrated acetic acid by slight heating. Pour the clear solution into 80 ml. of water and dilute to 100 ml.

Procedure—Neutralise the uranium solution by adding dilute aqueous ammonia, until a faint turbidity persists or, if tartrate is present, to *p*H 6. Clear the solution by means of a few drops of 2 *N* hydrochloric acid, add 20 to 25 ml. of 20 per cent. ammonium acetate solution, and heat to boiling. Add, drop by drop while stirring, 0·5 ml. of the 4 per cent. oxine solution for each 10 mg. of uranium present, and 4 to 5 ml. in excess. As soon as the precipitate persists, stir until it becomes crystalline before adding more reagent. Finally add, dropwise with stirring, the same volume of *N* ammonia, in order to obtain a *p*H 5·2 to 5·8, and boil for 2 minutes. Allow to cool to 40° C. Filter through a sintered-glass crucible (Jena G4), and wash with 50 to 100 ml. of hot, 0·04 per cent., aqueous oxine solution. Dry at 110° to 140° C. for one to two hours, and weigh as the compound $UO_2(C_9H_6NO)_2.C_9H_7NO$, which contains 33·84 per cent. of uranium. For the volumetric determination, dissolve the dried precipitate in 2 *N* hydrochloric acid, and titrate with 0·05 to 0·2 *N* potassium bromate - potassium bromide solution in the usual way (R. Berg, "*Die Analytische Verwendung von o-Oxychinolin*," 2. Aufl. Stuttgart, 1938). The uranium oxinate can be ignited to U_3O_8 without the usual precaution of adding oxalic acid to prevent loss of oxinate by sublimation (*cf.* Kroupa, *Mikrochim. Acta*, 1938, **3**, 306). The dried precipitate is heated in an electric muffle, first at 1000° C., and then at 700° C. for one hour.

Results obtained by the gravimetric or volumetric procedures are 0·2 per cent. low for amounts of uranium greater than 50 mg., and accurate to 0·1 mg. for lesser amounts. When the oxinate is ignited and the uranium weighed as U_3O_8, the results obtained are accurate to within ±0·1 per cent. for up to 400 mg. of uranium. The slightly low results obtained by weighing the oxinate must be due to a small deficiency in the oxine content of the precipitate. Accuracy is unimpaired by the presence of several grams of tartaric acid, and complete separation from magnesium, calcium, strontium, and barium is obtained. B. A.

Determination of Gold with Ascorbic Acid. E. C. Stathis and H. C. Gatos (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 801)—The method is based on the reaction

$$2\ AuCl_3 + 3C_6H_8O_6 \longrightarrow 2Au + 3C_6H_6O_6 + 6HCl.$$

Procedure—Dissolve up to 0·3 g. of gold in *aqua regia* and evaporate to fuming with concentrated hydrochloric acid three times. Dissolve the residue in 3 to 5 ml. of concentrated hydrochloric acid and

dilute to 20 ml. with water. Heat the solution to between 80° and 90° C., and add 10 ml. of freshly prepared, 0·4 per cent. ascorbic acid solution; heat for 5 min. Allow to cool, and filter on to a porcelain filter crucible. Wash with diluted hydrochloric acid (1+99) and ignite.

Results show a maximum deviation of 1 in 290, the presence of up to equal amounts of copper being without effect.

Volumetric determination—The excess of ascorbic acid is titrated with iodine according to the scheme $C_6H_8O_6+I_2 \longrightarrow C_6H_6O_6+2HI$.

Procedure—Add to the gold solution, freed from oxidising agents, 2 to 5 ml. of concentrated hydrochloric acid and dilute to 20 ml. Add 10 ml. of ascorbic acid solution, stir for 5 min., add 2 ml. of starch solution, and titrate with 0·1 *N* iodine. Blank determinations must be made. A maximum deviation of 1 in 475 is recorded. M. E. D.

Detection of Ytterbium in Rare-earth Mixtures. G. Beck (*Helv. Chim. Acta*, 1946, **29**, 506–507)—The high reduction potential of bivalent ytterbium, produced by the action of magnesium or, better, sodium amalgam, enables it to reduce the carboxyl groups of certain organic acids to carbonyl groups which are easily detected as coloured derivatives. Oxalic acid is reduced to glyoxalic acid which forms a pink-coloured condensation product with naphthoresorcinol.

Procedure—Treat 1 to 2 ml. of an ice-cooled solution of the sulphates of the rare earths in dilute sulphuric acid with 0·5 ml. of sodium amalgam in a small separating funnel. When reduction is complete, remove the amalgam, and add 3 to 4 drops of boiled-out, saturated oxalic acid solution, to form not more than a slight turbidity. Add a small quantity of naphthoresorcinol and an equal volume of concentrated hydrochloric acid, heat to boiling for 1 to 2 min., cool, and dilute with water. On extraction of the solution with 1 to 2 ml. of ether, a pink coloration indicates the presence of ytterbium.

The reaction is not given by reduced titanium, europium, chromium, molybdenum, zirconium, or tantalum, but vanadium, uranium, niobium, and rhenium give positive results. Oxidising acids interfere, for divalent ytterbium is unstable, even in contact with air. Pyrogallol and sulphuric acid, or tryptophan and sulphuric acid, can be used instead of naphthoresorcinol and hydrochloric acid, and phthalic anhydride can replace oxalic acid. A distinct coloration is obtained with 3 μg. of ytterbium under optimum non-oxidising conditions. The test was negative with cerium earths and yttrium fractions, weakly positive with gadolinium fractions, and strongly positive with erbium preparations. If, after reduction with zinc and hydrochloric acid, the cacothelin test is negative, the reaction is specific for ytterbium. M. E. D.

Agricultural

The Morgan Method of Soil Testing. Part IV. Use of the Spekker Absorptiometer for Estimating Phosphate. J. Tinsley and N. H. Pizer (*J. Soc. Chem. Ind.*, 1946, **65**, 208–211)—Following the work on the direct estimation of potassium, an examination was made of the conditions required for the direct estimation of phosphate by means of the molybdenum-blue reaction, using 1 ml. of soil extract and the measuring and other apparatus found suitable for the potassium test (*Idem, ibid.*, 1945, **64**, 182). The universal extracting solution (U.E.S.) used by Morgan (Tinsley and Pizer, *loc. cit., Connecticut Agr. Expt. Sta.*, 1937, Bull. 392; 1939, Circ. 127) consists of a buffer mixture of sodium acetate and acetic acid having a *p*H of 4·8. Extracts of field soils usually contain from 0 to 10 p.p.m. of phosphorus in the form of phosphate with variable amounts of other ions and small amounts of organic matter. In Morgan's original method. Phosphate is estimated directly on a spot plate by formation of molybdenum blue with sodium molybdate and stannous oxalate, 0·5 ml. of soil extract being used and the volume being increased by addition of reagents to only 0·65 ml., so that the final concentration of phosphate in a small volume of U.E.S. at a final concentration of 0 to 8 p.p.m. of phosphorus, using 13-mm. diameter glass tubes for the formation and measurement of the colour. By contrast, the final concentration of phosphorus in the method of Truog and Meyer (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 136) is of the order 0 to 0·25 p.p.m. and measurement is made in 1-cm. or 4-cm. cells.

Considerable modification of Morgan's process was found necessary, and stannous chloride proved to be a more suitable reagent than stannous oxalate. Colour formation was most intense when the sodium molybdate reagent contained 1·5 *N* hydrochloric acid, but with calcareous soils false results might be obtained, apparently owing to the reduced acidity or to the raised *p*H and not to the presence of calcium. This is important since soil extracts contain variable and often high amounts of calcium. The error may be corrected by addition of sufficient hydrochloric acid to the sodium molybdate reagent. With ordinary U.E.S. and with stannous chloride at a concentration of 0·1 per cent. in 0·1 *N* hydrochloric acid, the intensity of the blue colour depends upon the amounts of sodium molybdate and hydrochloric acid in the molybdate reagent (Woods and Milton, *Ibid.*, 1941, **13**, 760). With calcium-neutralised U.E.S., the sodium molybdate in the reagent must not exceed 1 per cent. With 0·1 per cent. stannous chloride in 0·1 *N* hydrochloric acid and 1 per cent. sodium molybdate reagent, the

concentration of the hydrochloric acid in the latter may range from 2·0 to 2·5 *N* for standards in ordinary U.E.S. and should be exactly 2·5 *N* for calcium-neutralised U.E.S. For most soil extracts the best concentration of hydrochloric acid in the sodium molybdate reagent appears to be 2·5 *N*, and this reagent should give accurate results with extracts of acid soils and slightly high results with calcareous soils, a maximum positive error of 5 per cent. being obtained when the acetic acid is fully neutralised. A final *p*H of 0·36 to 0·18 appears to be desirable. Stannous chloride concentration may range from 0·05 to 0·15 per cent. with little effect on colour development, but 0·1 per cent. is preferable with soil extracts of high phosphate content, since at this concentration fading of the colour is inhibited. With 0·1 per cent. stannous chloride reagent and 1 per cent. sodium molybdate in 2·5 *N* hydrochloric acid, colour development reaches a maximum in 2 min. in standards and in most soil extracts and remains constant for 30 min.

If the drum readings on the Spekker absorptiometer are plotted against p.p.m. of phosphorus in standard solutions, the points fall on a straight line over the range 0 to 8 p.p.m., and the curves for standards in ordinary U.E.S. and calcium-neutralised U.E.S. are almost coincident.

Method—The following method was tentatively adopted for routine estimation of phosphate in Morgan soil extracts, the molybdenum-blue colour being developed and measured in 13-mm. diameter glass tubes as described for the determination of potassium. To prepare the stock phosphate solution, containing 100 p.p.m. of phosphorus, dissolve 0·57435 g. of Sörenson's salt ($Na_2HPO_4.2H_2O$) in U.E.S. and dilute to 1 litre. Thymol may be added as preservative. To prepare standard solutions, dilute the stock solution with U.E.S. The sodium molybdate reagent contains 1 per cent. of sodium molybdate ($Na_2MoO_4.2H_2O$) in exactly 2·5 *N* hydrochloric acid, and is stable for 2 months in a stoppered, brown-glass bottle. To prepare the stock stannous chloride solution dissolve 2·5 g. of stannous chloride ($SnCl_2.2H_2O$) in enough hydrochloric acid to give 5 *N* acid after dilution to 50 ml. with water; it is stable for 2 weeks when stored in a refrigerator. The working stannous chloride solution is a 50-fold dilution of the stock solution. The apparatus is as previously described for the estimation of potassium (Tinsley and Pizer, *loc. cit.*)

Procedure—Fix a wooden block holding the requisite number of tubes firmly on the platform of the shaker, measure 1 ml. of phosphorus standard or soil extract into each tube, pour 1 ml. of sodium molybdate reagent down the side of each tube, and shake the mixture for 15 sec. Add 0·5 ml. of stannous chloride reagent to each tube shaking immediately by hand to mix and then in the shaker for 10 sec. After the tubes have stood for 10 min., place them in turn in the special brass holder on the Spekker instrument and measure the intensity of the colour. A 10-ml. pipette, subdivided to 0·1 ml. and having two extra 1-ml. marks at the upper end to provide molybdate reagent for 10 extracts and 1 standard and to allow rejection of the first millilitre drawn in, is recommended for measuring the molybdate reagent and, for the same reason, a 5-ml. pipette subdivided to 0·01 ml. and having two extra 0·5 ml. marks at the upper end is recommended for measuring the stannous chloride reagent. Warm the lamp of the instrument by switching on for 30 sec. and off for 15 sec., and repeating this four times. Use No. 1 red filters and place a tube containing water in the special brass holder against the lens holder on the right. Set the diaphragm at 1·5 on the drum with maximum sensitivity control and reduce the deflexion to zero. Construct the calibration curve as for potassium with 90 selected tubes to carry out 10 independent measurements with each of nine standards (0·5, 1·0, 2·0, . . . 8·0 p.p.m.). Multiply the mean drum reading for each set of standards by 100 and deduct this figure from 150 (the position of zero setting). Since the scale is logarithmic, this value is directly related to the phosphorus content. The calibration curve is a straight line from 1 to 8 p.p.m., but changes slope somewhat from 0 to 1 p.p.m. The curve obtained when 1-cm. optical glass cells are used is a straight line from 0 to 8 p.p.m. In routine determinations ten soil extracts are measured at a time, and one standard, usually in the range 5 to 6 p.p.m., is included as a check on the reagents and instrument. Day-to-day agreement with the curve is good and re-calibration is not necessary for months unless changes occur in the photocells, or unless the lamp is changed.

Temperature changes over the range 5° to 30° C. have slight effects on colour development, but these are not important in routine work. The following ions when included in the standards had no measurable effect on colour development or stability even in amounts greater than those occuring in soil extracts: magnesium, manganese, metasilicate, and iron, but a final concentration of 40 p.p.m. of iron markedly reduced the intensity of the blue colour in standards containing more than 1 p.p.m. of phosphorus. A. O J.

Bacteriological

Procedure for the Characterisation of the Acetic Acid Bacteria. Parts I and II. J. Tošić and T. K. Walker (*J. Soc. Chem. Ind.*, 1946, **65**, 104–107, and 180–184)—In Part I consideration is given to the precautions that must be adopted in standardising conditions for the examination of cultures of *Acetobacter* species in order that comparisons may be obtained for diagnostic purposes. Bacteriologists who first described species of

Acetobacter studied their characteristics in a wide variety of media and early communications are notable for the omission of details that are essential to proper comparison. Standard media and technique are first described in Part I, and the behaviour of ten authentic cultures of named species of *Acetobacter* (obtained from the National Collection of Type Cultures at the Lister Institute) when submitted to the standardised examination is recorded in Part II.

The standard media include Standard Malt Wort (S.M.W.); S.M.W. containing 2 per cent., 1·5 per cent., and 0·5 per cent. of agar, the latter being employed for testing motility; S.M.W. containing gelatin; nutrient broth; broth agar and broth gelatin; yeast water media including carbohydrate, yeast water and corresponding agar; and glucose phosphate broth for the Voges-Proskauer reaction. Standard inoculation procedures are described in detail. Stock cultures are inoculated into S.M.W. and incubated at optimum temperatures for 72 hr., after which a second subculture is made, incubated for 48 hr., and used to inoculate a third subculture which, after 24 hr. incubation, is used to inoculate the test media.

Differentiation is based upon morphological, cultural, biochemical, and physiological characteristics, which are described in detail. In Part II, it is shown that colonial appearance on S.M.W. agar serves to distinguish *A. ascendens* and *A. capsulatum* from all other species, and that the last-named alone forms spreading colonies; that streak cultures also distinguish *A. capsulatum* and the group *A. acetigenum*, *A. pasteurianum*, and *A. xylinum*; the last three also give characteristic growth in yeast water. Growth in S.M.W. containing varying concentrations of ethyl alcohol sharply distinguishes *A. gluconicum*, which is intolerant of 6 per cent., from *A. acetosum* and *A. ascendens*, which tolerate 10 per cent., the other species falling between these two extremes. Acid formation in yeast water containing various carbohydrates serves to distinguish quite a number of species, *e.g.*, only two, *A. capsulatum* and *A. suboxidans*, produce acid from maltose; only two, *A. aceti* and *A. acetigenum*, produce no acid from arabinose; only one, *A. xylinum*, fails to form acid in ethylene glycol and three are distinguished by their ability to oxidise acetic acid; these are *A. acetigenum*, *A. ascendens*, and *A. aceti*. D. R. W.

Physical Methods, Apparatus, etc.

Effect of Sieve Loading on the Results of Sieve Analysis of Natural Sands. F. A. Shergold (*J. Soc. Chem. Ind.*, 1946, **65**, 245–249)—The amount of material put on to a sieve can seriously affect the accuracy of a sieve analysis, and samples should generally be as small as possible. The loading effect of a material on a particular sieve is largely determined by the proportion of "near-mesh" particles, *i.e.*, particles which are just small enough to pass through the mesh apertures, and is influenced by particle shape. Flaky material is slightly more difficult to sieve than a sample composed of equi-dimensional particles, and elongated particles are very difficult to sieve. It is much better to reduce the weight of the sample on a given sieve than to sieve for a longer time. If the sieves are not overloaded the customary 9-min. shaking need not be exceeded unless high accuracy is required. Theoretically, the effective load on a sieve depends on the number of "near-mesh" particles per aperture, but practical tests suggest that larger mesh sieves overload more easily than finer sieves at a given amplitude of the sieve-shaking motion. The particle-size distribution within the sample has an important effect on the loading of sieves, and it is necessary to assume that a high proportion of difficult particles are present when determining the sample weight. With a natural sand the sample weight should be such that, after sieving, not more than the following amounts remain on the respective sieves:

B.S. Sieve No.	7	14	25	52	100	200
Weight retained (g.)	150	100	70	50	35	25

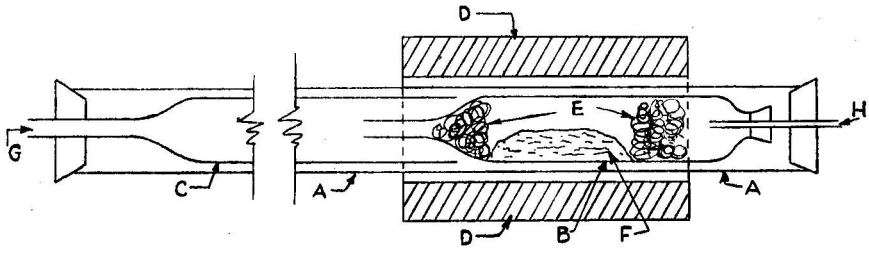
Values for intermediate sizes of sieves may be interpolated, but if the intermediate sieves are used in addition to those listed, all the weights should be halved as the proportion of "near-mesh" particles will be doubled. For crushed sands or rocks, smaller samples should be taken because of the less favourable particle shape. Usually, with natural sand, the original sample for the series of sieves listed is 100 to 150 g. for coarse sand and 40 to 60 g. for fine sand.

Recommendations based on the work described in this paper are incorporated in the revised British Standard for Concrete Aggregates (B.S. 882:1944, Appendix B). L. A. D.

Simple Sublimation Apparatus. J. Pitha (*J. Chem. Educ.*, 1946, **23**, 403)—The apparatus described is easy to construct and operate, and gives pure sublimates in good yield. The tube, A, is a 4-ft. length of 55 mm., O.D., Pyrex glass. The charge tube, B, is made by drawing out 45-mm. O.D., Pyrex tubing to a diameter of about 20 mm. at one end and tooling for a No. 8 rubber stopper at the other, the total length of the tube being about 2 ft. The collector tube, C, consists of about 20 in. of 45-mm. Pyrex tube sealed to a 12-in. length of 20 mm. tube at one end. The furnace, D, is wound on 18 in. of 2·5-in. leader pipe, and is covered with asbestos and rock-wool insulation, its construction allowing regulation of the temperature by a variable transformer.

Procedure—Place the tube, A, in the furnace and heat to the desired temperature. Introduce the

collecting tube into A and hold it in place by a rubber bung between the outer tube and the drawn-out end, then connect with a vacuum line or aspirator. Charge B with E, the material to be sublimed, glass wool plugs, E, being used to prevent spreading. Set the charged tube in place butting against the end of C, and adjust a gas delivery tube, H, through the stoppers in the ends of B and A. Gases may be passed through this tube, if desired.



The apparatus has been used to give good yields of highly-pure sublimates of arsenious oxide and phosphorus pentoxide. Crystalline selenium dioxide was obtained by using a stream of oxygen containing nitric oxide, a charge of 350 g. being sublimed in 90 min. The materials of which the apparatus is made must be modified for use at temperatures above 480° C., quartz or Vycor then being suitable.

M. E. D.

Reviews

FORENSIC CHEMISTRY. By HENRY T. F. RHODES, Dip.Inst.C. (Lyon). Pp. vii + 164. London: Chapman & Hall, Ltd., 1946. Price 15s. net.

In this book the author's general plan is to give a brief survey of the chemistry of each section of his subject, together with a collection of the appropriate, well-known (mostly qualitative micro-) analytical methods. From the purely analytical point of view, therefore, the book is likely to be of more use to the student of elementary forensic chemistry than to the expert analyst, who will find very little that is not already familiar to him. However, the latter will, as occasion arises, do well to consult it for much useful and interesting information of a non-analytical type, although the chemical treatment is, on the whole, elementary.

The ground covered is wide, as is evident from the chapter headings, *viz.*, direct and indirect identification of the person, stains, firearms and explosives, and the chemical examination of questioned documents, counterfeit money and toxic agents. The only notable omission (and one very difficult to account for) is textile fibres and fabrics, which receive brief treatment in 14 lines—and this despite the great amount and forensic importance of the knowledge now available concerning the chemical identification of fibres.

The title of the book has been followed strictly, perhaps too strictly in certain respects; thus, the use of ultra-violet light is very often much more rapid and convenient than chemical methods in dealing with stains, questioned documents, faded writing and sympathetic inks, but this fact may not be apparent to many of the readers to whom the book is addressed. With this (*i.e.*, the student) type of reader still in mind, the reviewer considers that the book would be improved by the inclusion of more working details of the analytical methods, and of illustrations; the absence of the latter is felt particularly in the sections dealing with fibres and with microchemical tests involving the formation of crystals of specific shapes.

There is much in the section on paper that the reviewer cannot agree with. In most cases the tests described will be less efficient than the human eye in dating a piece of paper or identifying it with another sample; the staining tests described are quite ineffective in distinguishing the majority of paper-making fibres, and need to be supplemented by microscopical examinations of structures; the sulphate content of paper is not a reliable indication of the presence of sulphite pulp (p. 101); artificial watermarks are by no means invariably removed by ether (p. 127); paper surfaces are not sized with rosin to produce smoothness (p. 102); organic pigments are confused with organic dyes on p. 104; good grade adhesives give neither a starch reaction with iodine nor do they appreciably reduce Fehling's solution (p. 123).

There is also a sprinkling of spelling errors, and the well-known test for nitrogen is referred to as the "black ring test" (p. 70). The style is clear, and the book is well documented with references to the sources from which information is drawn and with titles for further reading—a useful feature. It is indeed unfortunate that the defects noted above have to be recorded, but they can be rectified in the future edition that is bound to be called for.

The book is well produced, though when one bears in mind its size, the absence of illustrations and the fact that it is a second edition, the price must definitely be regarded as on the high side.

JULIUS GRANT

PHYSICAL METHODS GROUP

THE next meeting of the Physical Methods Group will be held in the Chemistry Lecture Theatre at King's College, Newcastle-upon-Tyne, at 6 p.m. on Friday, May 2nd, 1947. The following short papers on Physical Methods of Gas Analysis will be read and discussed:

"Gas Analysis at Low Pressures." By C. E. Ransley, M.Sc., Ph.D.

"The Analysis of Hydrocarbon Gases by Low Temperature Distillation." By J. H. D. Hooper, B.Sc., A.R.I.C.

"A New Apparatus for Gas Analysis by the Soap Film Method." By W. J. Gooderham, B.Sc., A.R.C.S., F.R.I.C., M.Inst.Gas E. Mr. Gooderham will demonstrate his apparatus.

Facilities will be available for a limited number of Members and visitors to take tea at King's College at 5 p.m. Members wishing to do this must advise Dr. J. O. Harris, Chemistry Department, King's College, Newcastle-upon-Tyne, 1, before Friday, April 25th.

POLAROGRAPHIC DISCUSSION PANEL

THE first ordinary meeting of the Polarographic Discussion Panel will be held at the Imperial College of Science and Technology, Imperial Institute Road, South Kensington, London, S.W.7, at 3 p.m. on Friday, April 25th, 1947, when a general discussion on Polarographic Analysis will be opened by Dr. W. Cule Davies, Dr. G. Jessop, and Dr. D. R. Roberts. Full details will be circulated to Members of the Polarographic Discussion Panel. Members of the Physical Methods Group who wish to become members of the Polarographic Discussion Panel are asked to inform Mr. J. T. Stock, the Honorary Secretary of the Panel, at the Chemistry Department, L.C.C. Norwood Technical Institute, Knight's Hill, London, S.E.27.