THE ANALYST

The Effect of Random Balance Errors in the Calibration of a Set of Weights

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In calibrating weights by intercomparison, analysts generally ignore errors arising from random fluctuations in the behaviour of the balance. It is shown that errors from this source may be, for a single weight, as large as twice the standard deviation for a single weighing on the balance used, and for a combination of weights, four times the standard deviation (at the 95 per cent. confidence limits). Means of reducing the error are suggested.

IT is customary in textbooks of analytical chemistry to discuss calibration of weights solely in terms of the traditional Richards' method[1] of intercomparison. No account is taken of errors that may arise from the statistical error inherent in each weighing made in the calibration. In a paper[2] on the calibration of weights of automatic weight-loading balances, it has been pointed out that these errors can be minimised by calibrating the weights against standard weights on a balance of greater sensitivity, though this procedure is cumbersome and is best replaced by one in which the weight combinations are calibrated *in situ* by a technique that yields maximum information for minimum effort.[2 to 6] So far, however, there has been no appraisal of the random errors likely to occur in the classical calibration procedure. In this paper, we have considered the intercomparison of a "5,3,2,1" set of weights from 10 mg to 10 g; a graticule will be regarded as equivalent to a rider.

Table I shows the nominal values of the weights placed in the two pans of the balance for each of the fourteen weighings that comprise the calibration. R denotes the nominal effective weight in milligrams of the rider when it is on the 10-mg scale reading, or the difference in pan load when the graticule projection reads 10 mg.

TABLE I

DESCRIPTION OF THE FOURTEEN WEIGHINGS

Weighing	Left pan, mg	Right pan, mg	Observed weight difference, mg
1	10	R	d_1
2	20	$10 + R$	d_2
3	20 + 10	30	d_3
4	30 + 20	50	d_4
5	50 + 30 + 20	100	d_5
6	100 + 50 + 30 + 20	200	d_6
7	200 + 100	300	d_7
8	300 + 200	500	d_8
9	500 + 300 + 200	1000	d_9
10	1000 + 500 + 300 + 200	2000	d_{10}
11	2000 + 1000	3000	d_{11}
12	3000 + 2000	5000	d_{12}
13	5000 + 3000 + 2000	10,000	d_{13}
14	10,000 standard weight	10,000	d_{14}

The correction in milligrams to be applied to the nominal weights will be written C_R for the rider or for 10-mg deflection on a graticule, C_{10}, C_{20}, . . ., C_{500} for the 10-, 20-, . . ., 500-mg weights, C_1', C_2', C_3', C_5', C_{10}' for the 1-, 2-, 3-, 5- and 10-g weights and C_S for the 10-g standard

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weight. Equating the observed differences in weight to the corresponding differences in the corrections gives the equations—

$$
\begin{aligned}
d_1 &= C_{10} - C_R \\
d_2 &= C_{20} - C_{10} - C_R \\
d_3 &= C_{20} + C_{10} - C_{30} \\
d_4 &= C_{30} + C_{20} - C_{50} \\
d_5 &= C_{50} + C_{30} + C_{20} - C_{100} \\
d_6 &= C_{100} + C_{50} + C_{30} + C_{20} - C_{200} \\
d_7 &= C_{200} + C_{100} - C_{300}
\end{aligned}
\qquad
\begin{aligned}
d_8 &= C_{300} + C_{200} - C_{500} \\
d_9 &= C_{500} + C_{300} + C_{200} - C_1' \\
d_{10} &= C_1' + C_{500} + C_{300} + C_{200} - C_2' \\
d_{11} &= C_2' + C_1' - C_3' \\
d_{12} &= C_3' + C_2' - C_5' \\
d_{13} &= C_5' + C_3' + C_2' - C_{10}' \\
d_{14} &= C_8 - C_{10}'
\end{aligned}
$$

Each correction can in turn be expressed in terms of C_R and the various values of d. The last equation can be used to express C_R as a function of the values of d, and this can be substituted in all the other equations to express each correction as a linear combination of the fourteen d values. The coefficients of these linear combinations are shown in Table II. The blanks in the table represent zeros.

TABLE II

THE COEFFICIENTS OF THE VALUES OF d IN THE FORMULA FOR THE CORRECTIONS

	d_1	d_2	d_3	d_4	d_5	d_6	d_7
C_R	−0·6	−0·4	+0·2	+0·1	+0·06	+0·04	+0·02
C_{10}	+0·4	−0·4	+0·2	+0·1	+0·06	+0·04	+0·02
C_{20}	−0·2	+0·2	+0·4	+0·2	+0·12	+0·08	+0·04
C_{30}	+0·2	−0·2	−0·4	+0·3	+0·18	+0·12	+0·06
C_{50}	—	—	—	−0·5	+0·3	+0·2	+0·1
C_{100}	—	—	—	—	−0·4	+0·4	+0·2
C_{200}	—	—	—	—	+0·2	−0·2	+0·4
C_{300}	—	—	—	—	−0·2	+0·2	−0·4
C_{500}	—	—	—	—	—	—	—
C_1'	—	—	—	—	—	—	—
C_2'	—	—	—	—	—	—	—
C_3'	—	—	—	—	—	—	—
C_5'	—	—	—	—	—	—	—
C_{10}'	—	—	—	—	—	—	—

	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	$(d_{14} - C_8)$
C_R	+0·01	+0·006	+0·004	+0·002	+0·001	+0·001	−0·001
C_{10}	+0·01	+0·006	+0·004	+0·002	+0·001	+0·001	−0·001
C_{20}	+0·02	+0·012	+0·008	+0·004	+0·002	+0·002	−0·002
C_{30}	+0·03	+0·018	+0·012	+0·006	+0·003	+0·003	−0·003
C_{50}	+0·05	+0·03	+0·02	+0·01	+0·005	+0·005	−0·005
C_{100}	+0·1	+0·06	+0·04	+0·02	+0·01	+0·01	−0·01
C_{200}	+0·2	+0·12	+0·08	+0·04	+0·02	+0·02	−0·02
C_{300}	+0·3	+0·18	+0·12	+0·06	+0·03	+0·03	−0·03
C_{500}	−0·5	+0·3	+0·2	+0·1	+0·05	+0·05	−0·05
C_1'	—	−0·4	+0·4	+0·2	+0·1	+0·1	−0·1
C_2'	—	+0·2	−0·2	+0·4	+0·2	+0·2	−0·2
C_3'	—	−0·2	+0·2	−0·4	+0·3	+0·3	−0·3
C_5'	—	—	—	—	−0·5	+0·5	−0·5
C_{10}'	—	—	—	—	—	—	−1·0

If each weighing is independent and subject to the same error variance, σ^2, irrespective of the total weight involved, then the error variance of a correction will be the sum of the squares of the coefficients of d multiplied by σ^2. Similarly, the error covariance of any two corrections will be the sum of the products of the corresponding coefficients of d multiplied by σ^2. These variances and covariances can be used to calculate the error variance of the total correction to be applied to any particular combination of weights. The error variances of the corrections for various total weights between 10 mg and 10 g are shown in Table III. The combinations of weights used are always those that involve the least number of weights (*i.e.*, 60 = 50 + 10 not 30 + 20 + 10). The variance of any other combination of weights can most easily be calculated by summing the appropriate coefficients of each value of d in Table II, squaring these sums and adding them and then multiplying the total by σ^2. The largest variance is probably that for 9990 mg (= 5000 + 3000 + 1000 + 500 + 300 + 100 + 50 + 30 + 10) and is—

$$4{\cdot}6838\sigma^2$$

The variance of the end results of a series of calculations involving additions and subtractions

of individual weighings can be calculated in a similar way. Approximate formula can also be derived for the variance of the end results of calculations involving products and quotients of individual weighings.

TABLE III

VARIANCES OF CORRECTIONS DIVIDED BY σ^2

Weight, mg	Variance divided by σ^2	Weight, mg	Variance divided by σ^2	Weight, mg	Variance divided by σ^2
R	0·5758	—	—	—	—
10	0·3758	100	0·3759	1000	0·3900
20	0·3030	200	0·3036	2000	0·3600
30	0·3818	300	0·3831	3000	0·5100
40	1·0121	400	1·0144	4000	1·2400
50	0·3940	500	0·3975	5000	0·7500
60	0·7273	600	0·7324	6000	1·2400
70	0·6122	700	0·6191	7000	1·3100
80	0·6486	800	0·6576	8000	1·5600
90	1·2365	900	1·2479	9000	2·3900
				10,000	1·0000

In Table III, the variances for weighings involving the use of a single weight are all less than or equal to σ^2, and (except for R, 3000 mg, 5000 mg and 10,000 mg) all lie between $0{\cdot}30$ and $0{\cdot}40\sigma^2$. The variances for weighings involving combinations of weights are often considerably larger. It will be seen from Table III that at the 95 per cent. confidence limits the random error for a single weight may be as much as twice the standard deviation for a single weighing, and, for a combination of weights, four times the standard deviation; for any combination of weights the error (at the same confidence limits) exceeds one standard deviation. The standard error for a single weighing of an object that involves the use of a weight combination with an error variance of $\alpha\sigma^2$ will be $\sigma\sqrt{1+\alpha}$. Therefore, 95 per cent. of such weighings should be within about $\pm 2\sigma\sqrt{1+\alpha}$ of their true value. Repeated weighings of the object x times will reduce the standard error to $\sigma\sqrt{\frac{1}{x}+\alpha}$. The values of α could be reduced—

(*i*) by replicating some of the calibration weighings,

(*ii*) by including more standard weights in the calibration,

or (*iii*) by weighing different combinations of weights against each other and, in particular, by including some weighings in which there are more than one weight in both pans. The corresponding equations relating the corrections to the d values would be more complicated, but could be obtained by applying the theory of least squares.

NOTES

It has been assumed that the 10-g standard weight has been tested by the National Physics Laboratory and has an error of ± 10 μg (95 per cent. confidence) in its quoted value (equivalent to a standard deviation of 5 μg). If the standard deviation for the balance is greater than 0·03 mg, no significant error is introduced by ignoring this error in the quoted value. If the standard deviation for the balance is less than 0·03 mg, the random errors in the calibration will not be significant in comparison with the likely size of the corrections to be applied to weights used on an ordinary balance. If the standard deviation of the balance is large compared with that assumed for the error of the standard weight the latter standard deviation can be ignored. If it is small, however, allowance should be made for the uncertainty in the value of the standard, and if this is done by simple proportion the effect will be significant only for weights of more than 1 g used on microbalances.

The corrections given are the relative errors for the particular set of weights used on the right-hand pan of a particular balance. If the absolute errors are required, then the ratio, l to r, of the lengths l and r of the left-hand and right-hand arms of the beam, respectively, must be taken into account. The ratio can be determined by transpositional weighing of

two large weights, and the values of the differences calculated accordingly. The corrected difference, d'_n, is given by—

$$d'_n = d_n - \left(\frac{l}{r} - 1\right) \times \text{nominal weight tested.}$$

References

1. Richards, T. W., *J. Amer. Chem. Soc.*, 1900, **22**, 144.
2. Lester, C. J. E., and Williams, E. J., *Technical Paper* 0/11 (Mimeo), C.S.I.R.O., Australian Division of Forest Products, 1953.
3. Bell, G. A., *Technical Paper No.* 6, C.S.I.R.O., Australian National Standards Laboratory, 1955.
4. Humphries, J. W., *Aust. J. Appl. Sci.*, 1960, **11**, 360.
5. Lashof, T. W., and Macurdy, L. B., *Anal. Chem.*, 1954, **26**, 707.
6. Almer, H. E., Macurdy, L. B., Peiser, H. S., and Week, E. A., *J. Res. Nat. Bur. Stand.*, 1962, **66C**, 33.

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The Titrimetric and Spectrophotometric Determination of the Oxidising Capacity of Manganese Compounds

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A simple, reliable method that is more rapid than existing procedures is described for determining the oxidising capacity of manganese ores. Decomposition of the material is effected by vanadium^{IV} and hydrofluoric acid at room temperature without an inert atmosphere, so that the method is suitable for batch analysis. Vanadium ions are completely stable under these experimental conditions. Both a direct titrimetric and a photometric finish are used, the latter being based on the oxidation of *o*-dianisidine by vanadium^{V} formed during decomposition. In the colorimetric method, interference by iron^{III} is eliminated by the use of orthophosphoric acid. Results are compared with those obtained by using a standard method.

Iron, manganese, titanium, cerium, vanadium and uranium are multivalent elements that frequently occur in both natural and synthetic materials; consequently oxide and silicate materials containing these elements will generally possess either an oxidising or a reducing capacity. For example, in silicate rocks iron is often present in the reduced form, and several methods are available for determining the ferrous iron present in these materials.[1,2,3,4] Manganese is commonly found in the oxidised quadrivalent and tervalent states in its ores and minerals.

Several terms, such as "available," "excess," "active" and "surplus oxygen," have been introduced to describe the "oxidising capacity" of materials, but we prefer this latter term, which is similar to the term "oxidation capacity" introduced by Jonker.[5]

Knowledge of the oxidising or reducing capacity of a material may be required to determine the mineral type, to obtain a useful summation of a complete chemical analysis or to evaluate the usefulness of a material for industrial applications, for example, manganese dioxide ore as a de-polariser for dry cells, and transition-metal oxides as semi-conductors.

Several methods are available for determining the oxidising capacity of a material, and in each of these decomposition is effected by acids containing an excess of a reducing reagent. A direct determination by simple acid decomposition is not generally possible, since ions in high oxidation states are not sufficiently stable under these conditions.

In Bunsen's[6] chlorine-evolution method, iodine is liberated from iodide after distillation. Mgrudich and Clark[7] do not consider the method accurate, but Pantony and Siddiqi[8] in a recent critical study consider that, with proper attention to detail, it is the most accurate method for determining oxidising capacity. However, of all the methods available, it is easily the most time consuming; it requires a well designed distillation apparatus operating under an inert atmosphere, and, according to Kolthoff and Belcher,[9] it yields accurate results only after painstaking attention to detail. A simplification of the Bunsen method, that avoids the distillation stage, is the direct iodide method of Pickering[10] and Diehl.[11] This method is only satisfactory for materials that readily decompose, and according to Pantony and Siddiqi[8] yields slightly high results. Sachse[12] has modified this method for sealed-tube digestion. The widely used ferrous sulphate method of Level and Poggiale as modified by Lunge[13] requires the use of an inert atmosphere to prevent oxidation of the reagent by air. Another commonly used and convenient method, ascribed to Fresenius and Will by Treadwell and Hall,[13] and Lux,[14] has been criticised by Kolthoff and Sandell[15] and by Katz, Clarke and Nye[16] on the ground that catalytic decomposition of oxalate by manganous salts occurs. Pantony and Siddiqi[8] report high results. Other methods that have been proposed are the arsenite method of Cantoni[17] and the hydrogen peroxide method of Shaeffer.[18] Ingamells[19] used orthophosphoric acid containing manganous salts to decompose manganese minerals and reports that under these conditions the manganic ions formed are stabilised.

As both the common simple methods (the iodide and oxalate procedures) give high results for the oxidising capacities of manganese minerals, there is need for an improved simple procedure. According to Pantony and Siddiqi,[8] the positive error in this determination is due to an absorbed layer of oxygen on the surface of the powdered sample, an error that is reduced by using reagents with higher positive standard potentials. The standard reduction potential of the vanadium^{IV} - vanadium^{V} system is +1·0 V, and is thus more positive than those of the iron^{II} - iron^{III} (+0·77 V), iodide - iodine (+0·55 V) and oxalate (−0·49 V) systems; vanadium salts should therefore be superior to these other reagents. Studies have been made of the stability of vanadium ions under different acid conditions; in hot, concentrated sulphuric acid vanadium^{V} decomposes slightly,[2,3] but is completely stable in cold hydrofluoric acid. Recently methods have been proposed for determining the oxidising capacity of various materials by using vanadium^{IV} in a hot, dilute sulphuric acid medium,[20,21] but decomposition times are limited because of the slight instability of the generated vanadium^{V} in hot sulphuric acid.[2,3] I have found that manganese ores and minerals are readily soluble in cold hydrofluoric acid containing an excess of vanadyl sulphate, and that both vanadium^{IV} and vanadium^{V} are indefinitely stable under these conditions. These observations form the basis of an elegant titrimetric method for determining the oxidising capacity of manganese ores and minerals. Vanadium^{V} generated by oxidation of the vanadyl sulphate reagent is directly titrated by standard ammonium ferrous sulphate solution. An alternative finish, suitable for micro-determinations, is based on the oxidation by vanadium^{V} of a redox indicator to a coloured product that is measured spectrophotometrically.

This work is a continuation of my work on the analytical uses of vanadium salts in determining the reducing and oxidising capacities of various materials. Previous papers have dealt with the macro- and micro-determination of ferrous iron in rocks and minerals.[3,4]

Experimental

Dissolution of samples—

Two different acid media were used, in conjunction with vanadyl sulphate, for dissolving 100-mg samples of pyrolusite, hausmannite and purpurite. These were 30 ml of 4 N sulphuric acid near its boiling-point; 6 ml of cold hydrofluoric acid (1 + 1) were equally efficacious. The hydrofluoric acid procedure was more convenient for batch analysis and effected complete decomposition of siliceous materials, whereas the sulphuric acid attacked only the manganese mineral consituent of ores.

Stability of vanadium ions under various acid conditions—

Previously it was found that both vanadium^{IV} and vanadium^{V} were stable in cold hydrofluoric acid.[3,4] However, it was thought that in this application, manganese^{II} ions might act as a catalyst and promote decomposition of vanadium ions in solution as they do

Table I

Stability of vanadium ions in hydrofluoric acid solution containing manganese^{II} ions

Time of standing, days	Manganese sulphate ($MnSO_4.4H_2O$) added, mg	Vanadyl sulphate ($VOSO_4.3H_2O$) added, mg	Vanadium pentoxide (V_2O_5) added, mg	Vanadium pentoxide (V_2O_5) found, mg	Recovery, per cent.
1	150	Nil	297·8	298·1	100·1
1	150	Nil	297·6	297·6	100·0
3	250	Nil	198·8	198·9	100·0
3	250	Nil	198·6	198·8	100·1
3	250	Nil	197·6	197·4	99·9
9	250	Nil	198·1	198·1	100·0
9	250	Nil	200·4	200·2	99·9
1	250	750	Nil	Nil	—
3	250	750	Nil	Nil	—
9	250	750	Nil	Nil	—

oxalate ions.[15,16] It was decided to extend the earlier investigations into the stability of vanadium ions in hydrofluoric acid to the new conditions where manganese^{II} ions are present. The results of this additional study (see Table I) show that manganese^{II} ions have no effect on the stability of vanadium ions in hydrofluoric acid.

The stability of vanadium ions in almost boiling 4 N sulphuric acid was also studied, both in the presence and absence of manganese^{II} ions, as no previous work on this topic has been published. After prolonged digestion (8 hours) a little vanadium^{V} decomposed (see Table II), and the time that can be allowed for dissolution of the sample in this procedure is limited. The cold hydrofluoric acid method of decomposition was therefore adopted.

TABLE II

STABILITY OF VANADIUM IONS IN HOT SULPHURIC ACID

Time of standing, hours	Manganese sulphate ($MnSO_4.4H_2O$) added, mg	Vanadyl sulphate ($VOSO_4.3H_2O$) added, mg	Vanadium pentoxide (V_2O_5) added, mg	Vanadium pentoxide (V_2O_5) found, mg	Recovery, per cent.
8	—	250	Nil	Nil	—
8	—	250	Nil	Nil	—
2	—	—	90·9	90·7	99·8
2	40	—	90·9	91·0	100·1
8	—	—	90·9	90·3	99·3
8	—	—	91·0	90·5	99·5
8	—	—	90·9	90·5	99·6
8	40	—	91·0	90·8	99·8
8	20	—	45·5	45·2	99·3
50	—	—	91·0	89·4	98·2

TABLE III

EFFECT OF FOREIGN IONS ON THE COLORIMETRIC METHOD

Concentration of vanadium^{V}, N	Additional substance added	Mean optical density
4×10^{-5}	Nil	0·637
Nil	0·5 mg $VOSO_4.3H_2O$	0·000
4×10^{-5}	50 μg Mn^{II}	0·639
Nil	50 μg Mn^{II}	0·000
4×10^{-5}	2 mg Fe^{III}	0·637
Nil	2 mg Fe^{III}	0·000
4×10^{-5}	1 mg H_3BO_3, 0·8 mg HF	0·638
Nil	1 mg H_3BO_3, 0·8 mg HF	0·000
4×10^{-5}	2 mg Fe^{III}, 50 μg Mn^{II}, 1 mg H_3BO_3, 0·8 mg HF	0·640
Nil	0·5 mg $VOSO_4.3H_2O$, 2 mg Fe^{III}, 50 μg Mn^{II}, 1 mg H_3BO_3, 0·8 mg HF	0·000

THE COLORIMETRIC MICRO-DETERMINATION

Frequently minerals are only available in small amounts, and an adaption of the method to the micro scale is needed; for this a colorimetric finish is desirable. The vanadyl sulphate method can be adapted to a photometric procedure. The vanadium^{V} formed during the decomposition of the sample can be determined by its oxidising effect on organic redox indicators.

Lyle[22] has discussed the use of reagents of the benzidine series for determining oxidants, and recently Ariel and Manka[23] have made a detailed study of the use of *o*-dianisidine for this purpose. In sulphuric acid solution the colour change of the latter indicator is from colourless (reduced) to red (oxidised). Ariel and Manka recommend an acid concentration of 10 N; this is satisfactory, but in the present work a somewhat higher acid concentration (16 N) was found to be preferable, because of improved stability and colour development.

However, iron is frequently associated with manganese ores and minerals, so that interference is to be expected because of the slight colour of iron in sulphuric acid solution; for this reason an orthophosphoric acid medium was considered to be more suitable. Further, some sulphuric acid samples were found to contain a reducing substance (possibly sulphite) that interfered with the method.

A study of this colorimetric method in orthophosphoric acid solution showed that, with increasing acid concentration, the time for complete colour development decreased, the stability of the colour formed improved and the maximum optical density increased. These results are summarised in Fig. 1. In all subsequent work, the colour was formed in 8 M orthophosphoric acid.

Vanadium,^{IV} manganese, fluoride and borate, which are always present in the proposed method, and iron^{III} ions, which may sometimes be present in the sample, have no effect (see Table III).

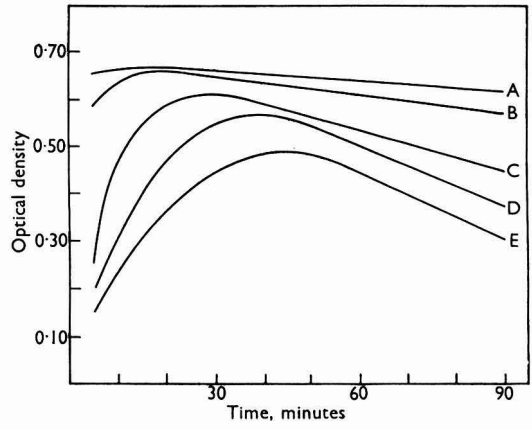

Fig. 1. The effect of time on the optical density of solutions containing 0·00004 N vanadium^{V} and 5 mg of *o*-diansidine hydrochloride in 25 ml of x M phosphoric acid. The optical density was measured at 456 mμ with the solutions in 1-cm cells. Curve A, $x = 8$; curve B, $x = 4$; curve *C*, $x = 2$; curve D, $x = 1$; curve E, $x = 0{\cdot}5$

The order of addition of reagents and sample solution affects the intensity of the colour developed. Maximum optical density was obtained when reagents were added in the order: orthophosphoric acid, *o*-diansidine solution, sample solution.

Preparation of the powdered sample

In the proposed procedures, only small amounts of ore or mineral powder are required. A sample of 100 mg suffices for the titrimetric method; sampling above this level would produce inconveniently high titres for ores rich in pyrolusite. In the colorimetric method the minimum sample size is governed, not by analytical considerations but by the sampling limitations discussed below. Manganese ores consist, in general, of at least two mineral components, and powdered specimens will in consequence be heterogeneous. It follows that the mineral composition of samples taken from a bulk powdered specimen will tend to deviate from the mean, and with small samples taken for chemical analysis this may be sufficient to affect the accuracy of the method.[24]

If the weight of sample taken is small, the sample must be ground sufficiently fine for the sampling error to be compatible with analytical accuracy.

To calculate sampling requirements we consider a specific example of the impure pyrolusite ore consisting of manganese dioxide contaminated with iron^{III} oxide. The sampling error, in terms of the standard deviation of manganese dioxide (MnO_2), s_E, is given by Wilson[24] as—

$$s_E = \sqrt{W_1 W_2 \left(\frac{d_1 d_2}{d}\right)\left(\frac{\bar{v}}{w}\right)} \text{ per cent.}$$

where W_1, W_2 are the percentage amounts of MnO_2 and Fe_2O_3,

d_1, d_2 are the densities of the mineral grains,

d is the mean density of the rock powder,

w is the weight of sample taken and

$\bar{v}$ is the weighted mean volume of the powder grains.

When $W_1 = W_2 = 50{\cdot}00$ per cent., the error will be a maximum, and so sampling errors for an ore of this composition are worth examination. If $d = d_1 = d_2 = 4{\cdot}8$, Table IV can be constructed.

TABLE IV

CALCULATION OF MAXIMUM ERROR FOR PYROLUSITE

Sample size, mg	Sieve size (B.S. mesh)	Error, in terms of standard deviation of MnO_2, per cent.	
		Maximum	Possible actual range
100	72	0·76	0·25 to 0·38
100	200	0·16	0·05 to 0·08
10	200	0·50	0·17 to 0·25

The maximum error is calculated on the assumption that all particles are of uniform size and equal in diameter to the sieve opening. The actual mean particles volume for average ground materials where there is a range of particle sizes will probably lie between 1/4 and 1/9 of the maximum particle volume. The possible range of error has been calculated by using these values.

Inspection of Table IV shows that 72-mesh powder is insufficiently fine for an accurate analysis. It appears that a sample of 100 mg of 200-mesh powder for the titrimetric method, and a sample of 10 mg of 200-mesh powder for the colorimetric method are compatible with the analytical accuracies to be expected. Accordingly, all ores were ground to 200 mesh for analysis. This is in agreement with the I.S.O. Recommendation (R312) that powders for "Active Oxygen" determinations should be less than 0·1 mm in diameter (about 150 mesh).

The fine grinding of rocks, minerals and ores may produce changes in chemical composition either by the heating effect of grinding or by surface adsorption, but little has appeared on this subject in the chemical literature. Hillebrand[25] has studied the effect of grinding on the water content and ferrous iron content of silicate rocks, and found that for some rock types prolonged grinding increased the combined water content by adsorption and decreased the ferrous iron content by oxidation. The effect of grinding manganese ores does not appear to have been studied, possibly because there is little effect. The thermal effect of grinding may be examined theoretically in terms of the thermal stability of manganese compounds in air. On these grounds it is doubtful whether grinding would effect the oxidising capacities of pyrolusites and hausmannites, since trimanganese tetroxide is probably the most stable oxide of manganese, and manganese dioxide is stable up to 530° C, at which temperature it begins to lose oxygen. Other manganese minerals are of less importance. Manganite is converted to pyrolusite when heated in air. Braunite is probably stable. Of the manganous minerals found in nature, the silicate, oxide and carbonate are oxidised on heating. From this it appears that grinding may either increase or decrease oxidising capacity, depending on the nature of the mineral, but that in practice this problem will not arise as the only significant effect, an increase in oxidising effect, is to be expected with the minerals manganosite (MnO) and manganite (MnO.OH).

Pantony and Siddiqi[8] have suggested that slight discrepancies between experimental results obtained by different methods are due to the adsorption of oxygen on the surface of mineral grains, and that this effect would therefore depend upon the state of subdivision of the powdered material. The presence of adsorbed oxygen effects those reagents subject to air oxidation, notably in the direct iodide and oxalate methods. The proposed method, like that of Bunsen, should not be affected by adsorbed oxygen.

The effect of fine grinding on manganese ores is not known with certainty, but in general it may be supposed to be small, and any error may be kept to a minimum by selecting a suitable chemical method and by a correct grinding technique. In this work, coarse powders were finely ground by hand. Grinding times were kept to a minimum by frequent sieving and by grinding only small amounts of sample at a time.

TITRIMETRIC METHOD

REAGENTS—

Vanadyl sulphate solution—Prepare a solution containing 25 per cent. w/v of vanadyl sulphate trihydrate, $VOSO_4.3H_2O$, in 2N sulphuric acid.

Standard ammonium ferrous sulphate solution.—Prepare a solution that is 0·05 N in 2 N sulphuric acid. A coil of pure aluminium wire (99·99 per cent.) immersed in this solution prevents deterioration and eliminates the necessity for periodic standardisations.

Hydrofluoric acid, 40 per cent. w/v.

Sulphuric acid, 20 N.

Indicator solution—Dissolve 0·3 g of barium diphenylamine sulphonate in 100 ml of water.

PROCEDURE—

Weigh out accurately about 100 mg of dried, finely ground (to 200 mesh) sample, transfer it to a plastic vessel and add vanadyl sulphate solution. The amount necessary to provide a sufficient excess depends on the oxidising capacity of the manganese mineral or ore body; for pyrolusites use 3 ml, for braunites use 2 ml and for hausmannites and other minerals use 1 ml. Add 3 ml of hydrofluoric acid and set the solution aside overnight. Most ores and minerals dissolve within a few hours, but an occasional resistant mineral may require 2 to 3 days' digestion.

When the sample has dissolved, add 10 ml of 20 N sulphuric acid and transfer the solution, by washing with water, to a 150-ml glass conical flask. Titrate the solution with the standard ammonium ferrous sulphate solution; use 5 drops of indicator solution. The colour change is from purple to green-blue.

Oxidising capacity (as oxygen), mg = 0·4000 × titre (ml) of 0·05 N ammonium ferrous sulphate solution.

COLORIMETRIC METHOD

REAGENTS—

Vanadyl sulphate solution—Prepare a solution containing 25 per cent. w/v of vanadyl sulphate trihydrate, $VOSO_4.3H_2O$, in 2 N sulphuric acid.

o-*Dianisidine hydrochloride solution*—Prepare a 0·5 per cent. w/v solution in 1 per cent. w/v acetic acid.

Hydrofluoric acid, 40 per cent. w/v.

Sulphuric acid, 20 N.

Orthophosphoric acid, 10 M.

Boric acid—Prepare a saturated aqueous solution.

Standard ammonium metavanadate solution—Prepare a 0·01 N solution from standardised analytical-reagent grade solid.

PROCEDURE—

Weigh out accurately about 10 mg of dried finely powdered (to 200 mesh) sample. For materials of lower oxidising capacity than pyrolusites, correspondingly more powder may be taken, up to 20 mg. Transfer the solid to a small plastic container and add 0·5 ml of vanadyl sulphate solution and then 0·5 ml of hydrofluoric acid. Set the mixture aside overnight, and after the sample has decomposed, add 10 ml of sulphuric acid and transfer the solution, by washing with water, into a 250-ml calibrated flask containing 10 ml of saturated boric acid. Dilute to the mark with water. For materials of low oxidising capacity a smaller calibrated flask may be used. Sample size and dilution should be selected so that the optical density of the final colorimetric solution does not exceed 0·7. Analyse appropriate standards and a blank solution at the same time. Omit the sampling and digestion stages and add an accurately measured volume of the standard ammonium vanadate solution (between 0 and 25 ml) and the reagents directly to a 250-ml calibrated flask. Dilute to the mark with water.

To a 25-ml calibrated flask add 20 ml of orthophosphoric acid and 1 ml of *o*-dianisidine hydrochloride solution, and mix them. Add a 1-ml portion of a control or sample solution from a pipette to the reagents, and mix them. Use the same 1-ml pipette for all control and sample solutions. Dilute to the mark with water, and mix the solution well. Measure

the optical density of solutions in a 1-cm cell at 456 mμ as soon as liberated air bubbles have dispersed.

TABLE V

COMPARISON OF RESULTS BY VARIOUS METHODS

Serial No.	Sample material	Oxidising capacity, as per cent. oxygen, by using— proposed titrimetric method	proposed colorimetric method	ammonium ferrous sulphate method	other laboratories (various methods)	Approximate time necessary for complete decomposition by proposed method
1	High-grade pyrolusite ore	16·44, 16·40, 16·47	16·4, 16·5	16·42, 16·47		2 minutes
2	High-grade pyrolusite ore	16·11, 16·12	16·0, 16·0	16·06, 16·02		6 hours
3	Manganese ore	3·00, 3·02	3·1, 3·1	3·02, 3·01		3 days
4	Pyrolusite ore	15·26, 15·21, 15·30	15·2	15·25, 15·23		5 minutes
5	Pyrolusite ore	15·31, 15·30	15·4	15·87, 15·26		10 minutes
6	Pyrolusite ore	13·25, 13·22	12·8	13·25, 13·22		6 hours
7	British Chemical Standard manganese ore 176/1	13·46, 13·52, 13·52	13·5, 13·5	—	13·43 to 13·56 (mean 13·50)	1 day
8	Hausmannite ore.. ..	5·59, 5·62	5·6, 5·7	5·59, 5·58		2 to 3 hours
9	Hausmannite ore.. ..	5·24, 5·25	5·4	5·29, 5·21		2 to 3 hours
10	Purpurite mineral ..	2·49, 2·49, 2·52	2·5, 2·6	2·50, 2·48		30 minutes
11	National Bureau of Standards manganese ore 25c	16·67, 16·66, 16·63	16·7, 16·8	—	16·70 (mean)	6 hours
	Theoretical values of oxidising capacity (as oxygen)	MnO_2, 18·40 per cent; Mn_3O_4, 6·92 per cent.				

RESULTS

The proposed titrimetric and the colorimetric procedures were applied to samples of pyrolusite and hausmannite ores and to a sample of pure purpurite mineral, $(Mn^{III}, Fe^{III})PO_4$, and the results obtained were compared with those obtained by using the ammonium ferrous sulphate method. The latter, a recommended I.S.O. method, has been shown by Pantony and Siddiqi[8] to be capable of giving results that are in good agreement with those obtained by using the Bunsen method. The results, summarised in Table V, show good agreement between the proposed methods and the standard ammonium ferrous sulphate method.

CONCLUSIONS

Vanadyl sulphate in hydrofluoric acid is a satisfactory reagent for determining the oxidising capacity of manganese minerals and has been used to develop an elegant and accurate titrimetric procedure. Correlation of results between this method and the ferrous salt method were good.

The proposed method is simpler than existing accurate procedures, since, in the ferrous salt method, digestion is conducted under an inert atmosphere and the chlorine-evolution method embodies a careful distillation technique. As heating is not required for digestion of the sample, manipulative time is reduced to a minimum and the method is suited to batch analysis.

For micro-scale determinations, there is the advantage that a colorimetric procedure is adaptable to the method.

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REFERENCES

1. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," Second Edition, John Wiley & Sons Inc., New York, 1953, p. 907.
2. Schein, A. V., *Zavod. Lab.*, 1937, **6**, 1199.
3. Wilson, A. D., *Analyst*, 1960, **85**, 823.
4. ——, *Bulletin of the Geological Survey of Great Britain*, 1955, No. 9, p. 56.
5. Jonker, G. H., *J. Phys. Chem. Solids*, 1959, **9**, 165.
6. Bunsen, R., *Annalen*, 1853, **86**, 265.
7. Mgrudich, J. N. and Clark, G. L., *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 256.
8. Pantony, D. A. and Siddiqi, A., *Talanta*, 1962, **9**, 811.
9. Kolthoff, I. N., and Belcher, R., "Volumetric Analysis," Second Edition, Interscience Publishers, New York and London, Volume III, 1957, p. 284.

10. Pickering, S. P. U., *J. Chem. Soc.*, 1880, **37**, 128.
11. Diehl, W., *Dinglers polytech. J.*, 1882, **246**, 196.
12. Sachse, H. B., *Anal. Chem.*, 1960, **32**, 529.
13. Treadwell, F. P., *translated and revised* Hall, W. T., "Analytical Chemistry," Ninth English Edition, John Wiley and Sons, London and New York, Volume II, 1942, p. 559.
14. Lux, F., *Z. anal. Chem.*, 1880, **19**, 153.
15. Kolthoff, I. N., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Revised Edition, Macmillan & Co. Ltd., London, 1950, p. 604.
16. Katz, M. J., Clarke, R. C., and Nye, W. F., *Anal. Chem.*, 1956, **28**, 507.
17. Cantoni, O., *Annali Chim. Appl.*, 1926, **16**, 439.
18. Shaeffer, J. A., *J. Ind. Eng. Chem.*, 1916, **8**, 237.
19. Ingamells, C. O., *Talanta*, 1960, **4**, 268.
20. "Report of the Government Chemist, 1962," H.M. Stationery Office, London, 1963, p. 47.
21. Wickham, D. G., and Whipple, E. R., *Talanta*, 1963, **10**, 314.
22. Lyle, S. J., *Ibid.*, 1959, **2**, 293.
23. Ariel, M., and Manka, J., *Anal. Chim. Acta*, 1961, **25**, 248.
24. Wilson, A. D., *Analyst*, 1964, **89**, 18.
25. Hillebrand, W. F., *J. Amer. Chem. Soc.*, 1908, **30**, 1120.

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Studies of the Separation of Trace Metals by the Manganese Dioxide "Collection" Method

Part II.* The Behaviour of Lead: Determination of Antimony and Tin in the Presence of Lead

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Studies of the effect of acid concentration upon the efficiency of the "collection" of lead by manganese dioxide co-precipitation are reported. The optimum acid concentration (0·008 M) has been established, and the concentration range over which the "collection" is quantitative has been found. Methods for determining tin and antimony in the presence of lead, both separately and in admixture, have been worked out. Tables of results showing recoveries are presented, and certain aspects are discussed.

In Part I of this series,[1] the development and application of the manganese dioxide "collection" method was traced from the original studies of Blumenthal[2] and Kallmann and Prestira,[3] and various applications of the procedure were mentioned.[4 to 9] It was noted that, in spite of widespread application, no systematic studies of the general applicability had been made. Studies were reported of the factors that affect the quantitative "collection" of bismuth, antimony and tin, and the effective concentration ranges for the co-precipitation of these species, both separately and in admixture, were defined. Methods were suggested for determining antimony and tin in the presence of large amounts of bismuth.

This paper describes a study of the conditions for the "collection" of lead, especially the effect of acidity of the solution on quantitative co-precipitation. Further studies were also made of the "collection" of tin and antimony, and from the results obtained conditions were established for determining these elements in the presence of lead.

Experimental

"Collection" of lead—

The "collection" procedure previously described[1] was used for all experiments. Brief details are given below—

Treat the sample solution in a 400-ml beaker with sufficient nitric acid solution to bring the volume up to 200 ml. Add 5 ml of 5 per cent. manganous sulphate solution and heat the solution to boiling. Add 2·5 ml of 1·25 per cent. potassium permanganate solution dropwise, and continue boiling for a further 2 minutes. Allow the solution to stand at a temperature of about 70° C for 30 minutes and then filter off the manganese dioxide precipitate on an 11-cm Whatman No. 40 filter-paper. Wash the precipitate three times with 10-ml portions of the nitric acid solution used for the initial dilution, using the first two washings to transfer the last traces of precipitate from the beaker to the filter-paper.

A series of 10-ml portions of a standard lead solution (prepared by dissolving pure lead nitrate in water so that the solution contained 2 mg of lead per ml) was subjected to the above "collection" procedure, in which 1·2 M nitric acid was used. The precipitate was dissolved and treated as described below, and the lead was determined polarographically.

Polarography was carried out at 25° C with a Tinsley Mark 19 polarograph. All potentials quoted are on the European sign convention. According to this convention, the potential of the saturated calomel electrode is taken as +0·246 V *versus* the normal hydrogen electrode.

Two procedures for dissolving the manganese dioxide precipitate were investigated.

(*i*) The precipitate and filter-paper were transferred to a 400-ml beaker and 3 ml of 18 M sulphuric acid and 5 ml of 16 M nitric acid added. The filter-paper was then destroyed

* For details of Part I of this series, see reference list, p. 586.

by repeated evaporation until a clear solution was obtained. During the evaporation further amounts of 16 M nitric acid were added as necessary. The resulting solution was transferred to a 250-ml calibrated flask and diluted to the mark with water. Fifty millilitres were then withdrawn, placed in a 100-ml calibrated flask, treated with 10 ml of N potassium chloride and diluted to the mark with water.

Portions of solutions prepared as above were de-oxygenated by passage of hydrogen gas for 15 minutes, and then polarographed. No steps for lead were obtained even at the maximum sensitivity of the polarograph, but severe interference, owing to early hydrogen discharge, was encountered.

(*ii*) The manganese dioxide precipitate was completely dissolved by allowing about 10 ml of a hot 20 + 1 mixture of 1·2 M nitric acid and 100-volume hydrogen peroxide to run down the sides of the filter-paper. The filter-paper was then washed with a further 15 ml of the nitric acid - hydrogen peroxide solution and finally with water. The solutions and washings were collected in a 400-ml beaker. After dilution to about 100 ml, the solution was boiled gently to liberate most of the excess of hydrogen peroxide. It was then allowed to cool and sulphur dioxide gas was bubbled through to convert residual hydrogen peroxide to sulphuric acid. The excess of sulphur dioxide was finally removed by boiling.

The solution was transferred to a 250-ml calibrated flask and diluted to the mark with water. Fifty millilitres of this solution were placed in a 100-ml calibrated flask, treated with 10 ml of N potassium chloride and diluted to the mark with water.

Polarography of this solution yielded a good step for lead of half-wave potential about −0·5 V. The step height, however, indicated that only a small fraction of the initial amount of lead (40 μg per ml of solution) was present. Therefore the "collection" of this element from 1·2 M nitric acid solution was concluded to be inefficient.

In view of the satisfactory nature of the polarographic step obtained, this method of dissolution was adopted for subsequent experiments.

EFFECT OF ACID CONCENTRATION ON THE "COLLECTION" OF LEAD—

A series of 10-ml portions of the standard lead solution containing 2 mg of lead per ml of solution were diluted to 200 ml with various nitric acid solutions so that the final nitric acid concentration varied from 1·2 M downwards. The manganese dioxide "collection," dissolution and polarography were carried out on each solution exactly as recommended above. The results are presented in Table I. In this Table the amount of lead recovered and the percentage "collection" have been calculated from results obtained with standard lead solutions not subjected to the "collection" procedure.

TABLE I

EFFECT OF ACIDITY ON THE "COLLECTION" OF 20 mg OF ADDED LEAD

Nitric acid concentration, M	Step height*	Lead found, mg	"Collection," per cent.
1·2	21·5	0·82	4·1
1·2	18	0·72	3·6
0·8	32	1·28	6·4
0·8	31·5	1·26	6·3
0·4	43	1·72	8·6
0·4	42	1·68	8·4
0·2	62	2·48	12·4
0·2	59	2·36	11·8
0·08	68	2·72	13·6
0·08	70·5	2·82	14·1
0·04	360	14·4	72·0
0·04	345	13·8	69·0
0·02	395	15·8	79·0
0·02	400	16·0	80·0
0·01	405	16·2	81·0
0·01	412·5	16·5	82·5
0·008	442	17·7	88·4
0·008	435	17·4	87·0
0·004	422·5	16·9	84·5
0·004	430	17·2	86·0

* Step heights are in scale divisions of the Tinsley polarograph chart corrected to the 1-μA sensitivity setting of the instrument.

During the above experiment it was noted that, as the amount of lead collected increased with decreasing acidity a white precipitate formed on passage of sulphur dioxide. This was shown by simple qualitative analysis to be lead sulphite. Variations in the procedure such as boiling the solution for 15 minutes to remove the excess of hydrogen peroxide, and then passage of sulphur dioxide for only one minute failed to prevent the formation of this precipitate. It was therefore decided to add 15 ml of 16 M nitric acid to the solution just before passage of sulphur dioxide. This increase in the overall acid concentration effectively prevented formation of the precipitate without interference with the polarographic determination of lead.

The results in Table I show that the optimum nitric acid concentration for the collection of lead is about 0·008 M.

In order to investigate whether the apparent percentage recovery of lead could be improved, a series of experiments were carried out as before, with 0·008 M nitric acid, but with increased amounts of potassium permanganate. The results for the recovery of 20 mg of added lead are given below—

Volume of 1·25% $KMnO_4$ solution, ml	2·5	2·5	2·5	5·0	5·0	5·0	10·0	10·0
Lead found, mg	17·7	17·6	17·4	17·4	17·5	17·2	17·6	17·7

EFFECTIVE CONCENTRATION RANGE—

Studies to establish the lead concentration range over which the "collection" procedure is effective were made by subjecting standard lead solutions of various concentrations to the procedure used above. The results are given in Table II.

TABLE II

EFFECTIVE CONCENTRATION RANGE FOR RECOVERY OF LEAD

Lead added, mg	Step height*	Lead found, mg	"Collection," per cent.
0·5	12·0	0·48	96
0·5	12·5	0·495	99
1·0	25·5	1·02	102
1·0	25·0	1·00	100
5	121	4·84	96·8
5	123	4·92	98·4
10	245	9·8	98·0
10	242·5	9·7	97·0
15	340	13·6	90·7
15	335	13·4	89·3
20	442	17·7	88·4
20	435	17·4	87·0
25	512·5	20·5	82·0
25	515	20·6	82·4
30	575	23·0	76·6
30	582	23·2	77·2
40†	—	—	—

* Step heights are in scale divisions of the Tinsley polarograph chart corrected to the 1-μA sensitivity setting of the instrument.

† For solutions containing 40 mg of lead, precipitation occurred on heating with manganous sulphate before the addition of potassium permanganate.

DETERMINATION OF TIN IN THE PRESENCE OF LEAD—

The results presented in Table I showed that the amount of lead "collected" from solutions 1·2 M with respect to nitric acid, was negligible. It has already been established[1] that the "collection" of tin at this acid concentration is efficient. Experiments were therefore made to investigate the possibility of using this procedure to determine tin in the presence of lead.

Portions of standard solutions of tin and lead were placed in 400-ml beakers and diluted to 200 ml with 1·2 M nitric acid. The "collection" procedure was then carried out as already described and the manganese dioxide precipitate filtered off on a Whatman No. 40 filter-paper.

Dissolution of the precipitate by the nitric acid - hydrogen peroxide method used for lead was found to be unsatisfactory. The tin was frequently oxidised to the stannic state, leaving a white residue on the filter-paper. The wet oxidation procedure, mentioned earlier

and rejected for dissolving lead was therefore tried, with suitable modifications to provide a solution suitable for the polarography of tin.

Each filter-paper and manganese dioxide precipitate was placed in a beaker and treated with 3 ml of 18 M sulphuric acid and 5 ml of 16 M nitric acid. The filter-paper was then destroyed by repeated evaporation, further amounts of nitric acid being added as necessary. After oxidation of all carbon to give a clear solution, careful evaporation almost, but not quite, to dryness was carried out. The residue was allowed to cool, 15 ml of 36 per cent. hydrochloric acid was added and the solution diluted to 50 ml. After being heated for a few minutes, the residue dissolved to give a clear solution, which was transferred to a 250-ml calibrated flask and diluted to the mark with washings from the beaker.

Fifty millilitres of each solution were placed in a 100-ml calibrated flask, treated with 10 ml of 36 per cent. hydrochloric acid, 10 ml of N potassium chloride and 10 ml of 5 N sodium hydroxide and finally diluted to the mark with water. Portions were placed in polarographic cells, de-oxygenated by passage of hydrogen gas for 5 minutes and polarographed for tin.

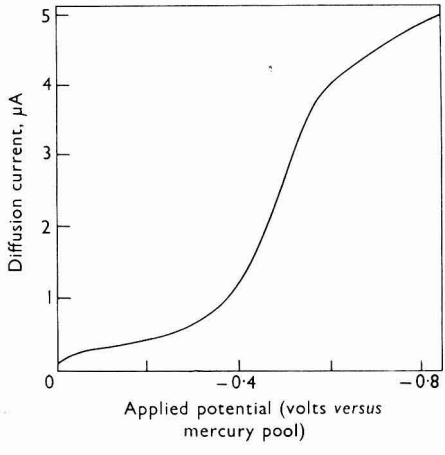

Fig. 1. Polarogram of tin in hydrochloric acid after manganese dioxide "collection" from a tin - lead solution

The calibration curve, prepared with standard tin solutions subjected to this procedure in the absence of lead, was a straight line passing through the origin. A typical tin step is shown in Fig. 1. Recoveries of tin from solutions containing lead are presented in Table III.

TABLE III

RECOVERY OF TIN FROM SOLUTIONS CONTAINING TIN AND LEAD

Tin added, mg	Lead added, mg	Tin found, mg
2	5	1·9
2	10	1·8
5	5	4·9
5	10	4·8
5	20	4·9
5	50	4·75
10	5	8·9
10	10	8·1
10	50	9·2
10	100	9·2
15	15	15·2
15	60	14·6
15	100	14·8

As previously noted, precipitation of lead occurred before the addition of potassium permanganate in all solutions of lead content higher than 30 mg. A preliminary filtration

was therefore necessary, the precipitate being washed with two 10-ml portions of 0·1 N sulphuric acid. The washings were added to the filtrate, and the manganese dioxide precipitation carried out as usual.

DETERMINATION OF ANTIMONY IN THE PRESENCE OF LEAD—

Previous results for the "collection" of antimony[1] had shown that, as for tin, a procedure for determining antimony in the presence of lead should be practicable. This was studied experimentally.

Portions of standard solutions of antimony and lead were placed in 400-ml beakers and diluted to 200 ml with 1·2 M nitric acid. The "collection" was then carried out as before, and the manganese dioxide precipitate filtered off on a Whatman No. 40 filter-paper. Dissolution of the precipitate was carried out by the nitric acid - hydrogen peroxide method used for lead, and the antimony was then determined absorptiometrically by the procedure given below, which has been described in full by MacNulty and Woollard[5]—

The solution of the manganese dioxide precipitate was placed in a 100-ml beaker, treated with 6 ml of 18 M sulphuric acid and covered with a watch glass. The beaker was heated carefully until the solution had evaporated to small bulk and then more strongly until dense fumes were evolved. After the beaker had cooled and the watch glass and sides of the beaker had been washed down with the minimum amount of water, the evaporation was repeated without allowing the solution to boil. It was then heated more strongly until dense fumes were again evolved. The evolution was continued for 2 minutes and the residue was finally allowed to cool.

One drop of 16 M nitric acid and 3 drops of 60 per cent. perchloric acid were added, and the beaker again heated on a hot plate. The solution became a deep purple and heating was continued until the colour faded and dense fumes were evolved. After 2 minutes further heating the beaker was allowed to cool. After the sides of the beaker had been washed down with about 5 ml of water this evaporation was repeated.

The beaker was transferred to an ice-bath and left for 30 minutes. The reagents required for the absorptiometric determination were also placed in the ice-bath at this time.

While the beaker was kept in ice, 6 ml of cooled constant-boiling hydrochloric acid was added, and the mixture allowed to stand for 5 minutes. Eight millilitres of cooled M orthophosphoric acid and 5 ml of cooled 0·04 per cent. Rhodamine B solution were then added. The mixture was transferred to a 75-ml separating funnel containing 10 ml of cooled benzene. After being shaken vigorously for 2 minutes, the benzene layer was run off into a 15-ml centrifuge tube and spun in a centrifuge for 30 seconds. The optical density of the solution was finally measured with a Spekker absorptiometer fitted with 1-cm cells and a yellow-green filter. A blank solution prepared as above, but containing no antimony was used as reference.

Antimony recoveries are given in Table IV.

TABLE IV

RECOVERIES OF ANTIMONY FROM SOLUTIONS CONTAINING ANTIMONY AND LEAD

Antimony added, mg	Lead added, mg	Antimony found, mg
1	5	0·8
1	10	0·85
5	20	4·9
5	50	5·0
10	50	9·0
10	100	9·3
20	50	18·5
20	100	18·8

For solutions containing more than 30 mg of lead, the preliminary filtration, described in the determination of tin, was carried out before the manganese dioxide "collection."

DETERMINATION OF ANTIMONY AND TIN IN THE PRESENCE OF LEAD—

In order to provide a method for determining antimony and tin together in the presence of lead, a slightly modified procedure was adopted. Portions of standard solutions of antimony,

tin and lead were placed in 400-ml beakers, subjected to the "collection" procedure and the precipitate filtered off on a Whatman's No. 40 filter-paper.

It had already been shown that the sulphuric acid - nitric acid dissolution of the precipitate introduces sufficient organic material to interfere with the determination of antimony, whereas the nitric acid - hydrogen peroxide method sometimes causes the precipitation of tin. The procedure given below was therefore introduced—

The precipitate was dissolved by allowing about 10 ml of a hot 20 + 1 mixture of 1·2 M nitric acid and 100-volume hydrogen peroxide to run down the sides of the filter-paper. The bottom of the filter-paper was then pushed through with a glass rod and the washing carried out first with 15 ml of the nitric acid - hydrogen peroxide mixture and finally with water. The solution and washings were collected in a 250-ml beaker.

Sulphur dioxide was bubbled through the solution for 5 minutes to decompose the residual peroxide, 6 ml of 18 M sulphuric acid were added and the solution was carefully evaporated to small bulk. It was next heated more strongly until dense fumes were evolved, and then allowed to cool. After addition of sufficient water to dissolve all the residue, the solution was transferred quantitatively to a 100-ml calibrated flask and diluted to the mark with water. This was then divided accurately into two 50-ml portions that were used for the separate determination of tin and antimony.

(*i*) *Determination of tin*—One 50-ml portion of each solution thus prepared was placed in a 100-ml calibrated flask, treated with 20 ml of 36 per cent. hydrochloric acid, 10 ml of N potassium chloride and 10 ml of 3 N sodium hydroxide. It was then diluted to the mark with water. Portions were placed in polarographic cells, de-oxygenated for 5 minutes by passage of hydrogen gas and polarographed for tin.

(*ii*) *Determination of antimony*—The other 50-ml portion of each prepared solution was placed in a 100-ml beaker and subjected to the absorptiometric determination of antimony with Rhodamine B by the procedure of MacNulty and Woollard,[5] already described in detail above. The optical density of each solution was finally measured on a Spekker absorptiometer.

The recoveries obtained in these determinations are given in Table V.

TABLE V

RECOVERIES OF ANTIMONY AND TIN FROM SOLUTIONS CONTAINING ANTIMONY, TIN AND LEAD

Antimony added, mg	Tin added, mg	Lead added, mg	Antimony found, mg	Tin found, mg
2	2	10	1·9	1·85
2	2	20	1·85	1·8
5	5	20	4·8	4·9
5	5	50	5·05	4·85
10	10	50	9·2	9·45
10	10	100	9·3	9·4
20	10	100	18·7	9·2
20	15	100	18·75	14·6
20	20	100	18·55	13·25

For all solutions containing more than 30 mg of lead, the preliminary filtration and washing described in the determination of tin alone was carried out to remove the precipitated lead before the manganese dioxide "collection."

"COLLECTION" OF TIN FROM 0·008 M NITRIC ACID SOLUTIONS—

In order to examine the possibility of using the "collection" procedure in conjunction with solutions of low acidity to determine lead in the presence of tin, a few experiments were made to ascertain the efficiency of the collection of tin under these conditions.

Standard solutions of tin in 0·008 M nitric acid were subjected to the "collection" procedure as described for the determination of tin in the presence of lead. Tin recoveries, determined polarographically, are given below—

Tin added, mg	5	5	10	10
Tin found, mg	3·75	3·8	7·6	7·65

In view of the fact that the efficiency of the "collection" of tin from 0·008 M acid solutions

was shown by these results to be better than 75 per cent., it was evident that separation of lead and tin could not be achieved under these conditions. These experiments were therefore abandoned and no similar experiments with antimony were made.

Discussion

The results given in Tables I and II show that the "collection" of lead can only be achieved from solutions of low acidity. The best results were obtained with 0·008 M acid and no improvement was obtained with lower acid concentration. The efficiency of "collection" decreased slightly with increasing lead concentration, but this was shown to be reproducible. Increasing the concentration of potassium permanganate did not increase the efficiency of "collection," or the total amount of lead that could be "collected." It is inferred from Table II that the maximum amount of lead that can be "collected" quantitatively is approximately 10 mg. Table I shows that there is a sudden and large increase in the efficiency of "collection" when the acidity is decreased from 0·01 M to 0·04 M.

It has been shown that the inefficiency of the "collection" of lead from solutions of high acid concentration can be used as the basis of a method for determining tin and antimony in lead. Results presented in Tables III and IV show that recoveries of these elements are virtually unaffected by the presence of lead even when its concentration is considerably in excess of the element being determined. Although the amount of lead was not increased above 100 mg in these experiments, it should be possible to tolerate much larger amounts. This is partly because precipitation of lead as the insoluble lead sulphate takes place on addition of the manganese sulphate when the amount of lead present is greater than 30 mg. Thus the amount of lead present during the "collection" is never greater than this amount, however large the initial concentration. In theory therefore there is no upper limit to the weight of lead in the sample, but in practice co-precipitation will probably occur when the bulk of the lead precipitate is large. No evidence of this, however, was provided by our results.

The precipitation of lead sulphate from solutions containing more than 30 mg of lead necessitated a filtration to remove the precipitate before the addition of the potassium permanganate. This appeared to have no effect on the recoveries of tin and antimony within the concentration ranges studied.

A high concentration of chloride ions was necessary for the polarography of tin[10] to ensure that the species present was $[SnCl_6]^{2-}$. At low chloride ion concentrations the chloride ions are replaced by a sheath of water molecules, which gives rise to poorly shaped, irreversible steps.

The method for determining antimony by means of the antimony - Rhodamine B complex in benzene solution is well known, and has been described in detail by MacNulty and Woollard.[5] It is quite straightforward, provided that the removal of organic matter is complete and the antimony is oxidised to the quinquivalent state. This should be achieved by the evaporation with sulphuric acid and by the final treatment with perchloric acid. If, however, the presence of residual organic matter is suspected, the perchloric acid treatment must be repeated. If these conditions are not met, serious interference with the colour development will occur.

The necessity for different methods of dissolving the manganese dioxide precipitate caused the adoption of a compromise procedure. It was considered that, on balance, the possibility of precipitation of tin when the nitric acid - hydrogen peroxide method of dissolving the precipitate was used, was more acceptable than the serious effects of organic matter on the absorptiometric determination of antimony. The results given in Table V show that the method evolved is generally satisfactory. This was not unexpected since precipitation of tin is the exception rather than the rule. The nitric acid - hydrogen peroxide method was in fact used for tin in some of our earlier work[1] without serious ill effects. During this phase of the work it was, nevertheless, found that a few recoveries of tin were grossly in error. They were so rare, however, that they could be neglected. For analytical purposes, the possibility of serious inaccuracy can be virtually eliminated by carrying out determinations in duplicate. The probability that both duplicate solutions will be affected is extremely remote.

It is evident from this and earlier work that the manganese dioxide method of "collection" and concentration has considerable value and that it can be made selective by suitable choice of conditions. Studies of its applicability to other species and to the separation of other combinations of metals are in progress and will be reported in later papers in this series.

References

1. Ogden, D., and Reynolds, G. F., *Analyst*, 1964, **89**, 538.
2. Blumenthal, H., *Z. anal. Chem.*, 1928, **74**, 33.
3. Kallmann, S., and Prestira, F., *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 8.
4. Babko, A. F., and Shtokalo, M. I., *Zavod. Lab.*, 1955, **21**, 767.
5. MacNulty, B. J., and Woollard, L. D., *Anal. Chim. Acta*, 1955, **13**, 64.
6. Park, B., and Lewis, E. J., *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 182.
7. Yamazaki, Y., *Bunseki Kagaku*, 1957, **6**, 422.
8. Luke, C. L., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 625.
9. Rooney, R. C., *Analyst*, 1957, **82**, 619.
10. Lingane, J. J., *J. Amer. Chem. Soc.*, 1945, **67**, 1916.

NOTE—Reference 1 is to Part I of this series.

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Differential Electrolytic Potentiometry

Part XV.* The Macro- and Microcoulometry of Acid - Base Reactions

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Differential electrolytic potentiometry has been examined as a means of locating the end-point in the determination of strong and weak acids and bases by constant-current coulometry. The excellent response speed of antimony electrodes permits direct recording of the differential electrolytic potentiometric signal during continuous generation without loss of accuracy. On the macro scale, determination of 0·001 mole of acid at 3×10^{-4} M gives results comparing favourably with careful volumetric work in accuracy, speed and convenience. A simple, versatile 2-ml cell for micro-scale work is described in which as little as 10^{-7} mole of strong or weak acids at concentrations of 5×10^{-5} M has been rapidly and simply determined with an overall precision of ± 2 per cent. Micro or semi-micro amounts are readily determinable with an accuracy of about $\pm 0{\cdot}1$ per cent.

Differential electrolytic potentiometry has been applied to acid - base reactions in which antimony electrodes are used,[1 to 6] and gives results of the highest precision and accuracy by the volumetric method. It has also been applied to electron-transfer,[7] precipitation[8] and complexometric[9] reactions by the coulometric method, especially in sub-micro and sub-nanogram ($<10^{-9}$ g) determinations in volumes of 0·5 ml or less. By some as yet unexplained phenomenon, differential electrolytic potentiometry permits the location of end-points at concentrations many orders below those predictable from the reaction constants.[8,10] Such sensitivity cannot be expected from the unique system of the formation of solvent molecules,[5] but coulometry considerably ameliorates the problem of carbon dioxide absorption.[1,6] The present investigation covers both macro and micro scales, with emphasis on the differential electrolytic potentiometry rather than on the coulometry,[11] which is regarded as being sufficiently precise (R. M. Pearson and J. W. Skinner, private communication).

The determination of bases with anodically generated hydrogen ions gives excellent results with differential electrolytic potentiometry, but needs isolation of the counter cathode, and as the use of carbonate-free primary-standard base solutions is difficult, most of the work has been confined to determination of strong and weak acids with cathodically generated hydroxyl ions. The primary reactions at a platinum cathode are—

$$2H^+ + 2\epsilon \rightleftharpoons H_2 \quad (1)$$
$$2H_2O + 2\epsilon \rightleftharpoons H_2 + 2OH^- \quad (2)$$

and in oxygenated solution—

$$O_2 + 2H^+ + 2\epsilon \rightleftharpoons 2OH^- \quad (3)$$
$$O_2 + 2H_2O + 4\epsilon \rightleftharpoons 4OH^- \quad (4)$$

whereas if hydrogen peroxide were present, the reactions would be[12]—

$$H_2O_2 + 2\epsilon \rightleftharpoons 2OH^- \quad (5)$$
$$H_2O_2 + 2H^+ + 2\epsilon \rightleftharpoons 2H_2O \quad (6)$$

Reactions depicted by equations (1) to (6) result in identical coulometric yields in terms of consumption of hydrogen ions or production of hydroxyl ions, and will occur whenever the cathode is freely allowed to run negative on the passage of current. They will occur with 100 per cent. current efficiency only if the medium is completely free from other cathodically active ions that may further complicate matters by solvolytic reactions. The presence of such ions can lead to current efficiencies greater or less than 100 per cent. and

* For details of earlier parts of this series, see reference list, p. 593.

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constitutes the principal limitation of the method. The coulometric anode need not be isolated provided the anodic reaction does not involve any ions either cathodically active or that can influence pH. Deposition of bromide on a silver anode—

$$Ag + Br^- \rightleftharpoons AgBr + \epsilon \quad .. \quad .. \quad .. \quad .. \quad (7)$$

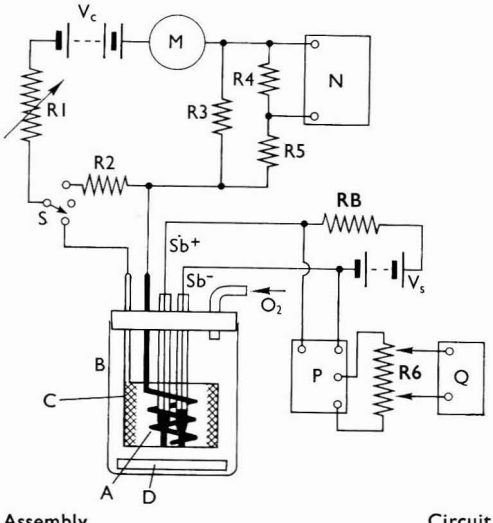
is suitable,[13] and it has been claimed[14] that the silver ion concentration resulting in the solution does not affect the cathodic current efficiency. This must be accepted with reservation, however, because the cathode becomes heavily coated with silver black if the bromide concentration is high, *e.g.*, 0·2 M, presumably through formation of $[AgBr_2]^-$, and at low bromide concentrations or current densities,[8] silver ions are stripped from the anode and may have a sufficient half-life to reach the cathode. At anodic current densities and bromide concentrations productive of a clean, porous, low-resistance silver bromide deposit,[15] no trouble is encountered and the claim is justified.

MACRO-DETERMINATION OF PERCHLORIC ACID

Experimental

Apparatus—

The assembly is conventional. In Fig. 1, the titration-vessel, B, is a 400-ml beaker with the top sawn off, fitted with a cover in which are rigidly mounted the differential antimony



Assembly		Circuit	
A	= Coulometric anode	R_1	= Decade resistors
B	= 400-ml beaker	R_2	= 200-ohm dummy-load resistor
C	= Generating cathode	R_3, R_4, R_5	= Standard 0·01 per cent. oil-immersed resistor chain: R_3, R_4 = 100-ohm resistors; R_5 = 1000-ohm resistor
D	= Magnetic stirrer	R_6	= Precision helipot
Sb^+, Sb^-	= differential antimony electrodes	R_B	= Ballast resistance
M	= Multirange ammeter	S	= Three-way switch
N	= Potentiometer	Vc	= Eight 120-V batteries in parallel
O_2	= Oxygen inlet	Vs	= 120-V source voltage
P	= pH meter		
Q	= 10-mV full-scale deflection chart recorder		
S	= Switch		

Fig. 1. Diagram of assembly and circuit for macrocoulometry

electrodes,[1,16] Sb^+ and Sb^-, the coulometric anode, A, made by coiling 14-s.w.g. pure silver wire on a mandrel, and the generating cathode, C, a conventional electro-deposition reinforced

platinum-gauze electrode (Johnson Matthey JM 72020) of 5-cm diameter. The generating electrodes must be rigid under the vigorous stirring conditions; use of a silver-foil anode led to superimposition of sinusoidal noise of considerable amplitude on the generating current. The differential electrolytic potentiometric electrodes are mounted within the silver anode so that they are out of the generating-current field, and are held in a separate plug, which is substituted for a blank plug in the cover when the indicating system is used. A polytetrafluoroethylene-coated magnetic-stirrer paddle, D, just shorter than the diameter of the beaker is used to produce maximum agitation. Carbon dioxide is excluded, and the solution oxygenated[6,16] by a stream of oxygen passing over the solution surface from the inlet tube, O_2, and escaping through small holes in the cover.

The differentiating circuit follows established practice. The source voltage, V_S, is commonly 120 V, and the ballast resistance, R_B, is selected to give the appropriate current density. Because of the high response speed of this electrode system, it is possible to record the signal continuously and also to use continuous instead of incremental[8] generation, and so that the time constants of the measuring instruments should not cause the extremely sharp differential peak normally obtained[1,6] to be missed, abnormally high current densities were used to produce the hump-shaped end-points whose maximum is determined geometrically by the classical method of Cailletet and Matthias. The differential potential, E_Δ, is measured on a direct-reading pH meter (E.I.L. 23A or 39A), P, having a recorder output that is applied to the calibrated precision helipot, R_6, from which the zero and span of the recorder (10-mV Cambridge D.E.) are set. A chart speed of 1 inch per minute is convenient. Deliberate introduction of noise into the recorder circuit ensures that the dead space does not interfere with indication.

The coulometric circuit is a higher-current version of that previously used.[7,8] Attempts to develop an electronic constant-current source from established circuits[17,18,19] have met with only limited success. The regulation and noise level achieved, while adequate for routine use, are not as good as expected. Instead, eight 120-V batteries, V_C, were used in parallel, from which 10 mA could be drawn for an hour or more without trouble from polarisation. This restriction of available current led to undesirably long generation times on the macro scale. With the 200-ohm dummy load, R_2, in circuit, the current, monitored on the multirange ammeter, M, is set by adjustment of the decade resistors, R_1. The current is accurately measured on the precision potentiometer (Doran M4989 or E.I.L. 39A), N, by the voltage drop in the standard 0·01 per cent. oil-immersed resistor chain, R_3 (100 ohms), R_4 (100 ohms) and R_5 (1000 ohms), for which other values are used as appropriate. Time is measured on flyback stopclocks, calibrated against the National Physical Laboratory standard frequency transmission on 4·4 Mc/s from Rugby and checked by the Post Office Telephones' "speaking clock." This crude arrangement is the principal limitation; precision would be greatly enhanced by proper time measurement.

REAGENTS—

Pure, carbon dioxide-free *water* as previously defined[1] is used throughout. The potassium bromide base electrolyte must be neutral; chloride impurity is without influence. Carbon dioxide-free 0·1 M perchloric acid solutions as previously described[1] were carefully standardised potentiometrically against dried, pure sodium carbonate,[5] and used to prepare more dilute solutions as required.

PROCEDURE—

The vessel is flushed with oxygen, weighed, 10 ml of carbon dioxide-free 0·01M perchloric acid added by pipette and the vessel re-weighed. Sufficient solid pure potassium bromide to give a final concentration of 0·05 M, and *water* to cover the electrodes (300 ml) are added. A continuous stream of oxygen is maintained. The antimony electrodes are not in place at this point. The generating current is switched through the dummy load and thermal equilibrium established at the selected current. The switch, S, is turned to bring the electrodes into circuit and the clock simultaneously started. Three alternative finishes are used.

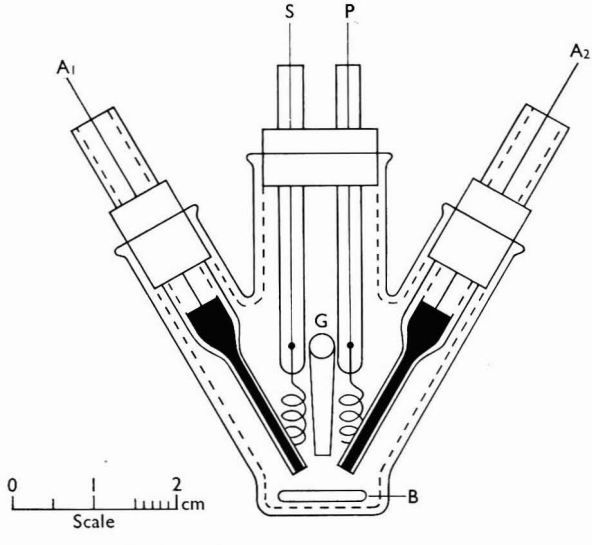
(*i*) About 10 to 15 per cent. before the equivalence point, the antimony electrodes are inserted, the recorder-chart drive started, and time markers placed on the chart by operation of the pH-meter switch. Generation is continued without interruption until the differential peak has been traversed.

(*ii*) Generation is interrupted at a convenient point 5 to 10 per cent. before equivalence, the antimony electrodes inserted, the recorder-chart drive started and the electrodes allowed to reach equilibrium. Clock and generation are restarted, the operation automatically providing a marker pip on the chart, and generation at the original current continued through the equivalence point as before.

(*iii*) Generation at the high current rate (2 to 10 mA) is stopped within 1 per cent. of equivalence, and the electrodes inserted and equilibrated as in (*ii*). Meanwhile, the generating current is re-adjusted on the dummy load to a lower value (0·2 to 0·5 mA). The determination is then concluded at the lower generation rate as in (*ii*). Throughout the generation, the current is measured at short intervals on a potentiometer, N. It has been found to remain constant to within $\pm 0{\cdot}01$ per cent.

Results and discussion

The method was developed for determining 1 millimole of perchloric acid at a concentration of about 0·0003 M. The accuracy was rather better than 0·1 per cent. The factor of the stock acid by the volumetric method was $0{\cdot}1027 \pm 0{\cdot}0002$ M, and by the coulometric method $0{\cdot}10269 \pm 0{\cdot}0001$ M; the maximum spread over some scores of determinations by methods (*i*), (*ii*) and (*iii*) and generating currents from 2 to 10 mA, corresponding to times from 80 to 16 minutes, is rather less than $\pm 0{\cdot}1$ per cent. Little difference in precision



A_1, A_2 = Antimony differential electrodes
S = Silver coulometric anode
P = Platinum coulometric cathode
G = Gas inlet
B = 10-mm magnetic stirrer

Fig. 2. Diagram of cell for semi-microcoulometry

between the different methods was revealed, though method (*iii*) was favoured for the highest currents. In the differential circuit, the electrode response speed was fast enough in method (*i*) even at high generating currents, and differentiating currents as high as 1 μA with an electrode area of 0·03 sq. cm gave smooth broad peaks that are easily interpreted. This differentiating current density of 30 μA per sq. cm is about 60 times the optimum recommended[1] for volumetric titration under similar conditions. The latter would give a peak breadth of less than 0·5 second under continuous generation at the higher currents that could be handled with appropriate equipment. With the time constants of the present equipment it was found more satisfactory to broaden the peak to 30 to 60 seconds. The traces are

similar to, though sharper than, those illustrated in Fig. 3 for micro-determinations. The method compares favourably in precision and convenience with the volumetric procedure.

MICRO-DETERMINATION OF STRONG AND WEAK ACIDS

Experimental

Apparatus—

After the development of small-scale titrimetric and coulometric cells,[7,8,10,20] a larger versatile cell was constructed to allow magnetic stirring, to accommodate any kind of differential and generating electrodes and to permit their interchange, and to permit the introduction of controlled atmospheres. The cell, shown in Fig. 2, is constructed from 15-mm Pyrex-glass tubing, with two side arms into which sheathed electrodes can be plugged, and a third side arm with an internal beak dipping into the liquid for the introduction of gas. Antimony micro electrodes[16] of cross-sectional area 0·0315 sq. cm are inserted in the side

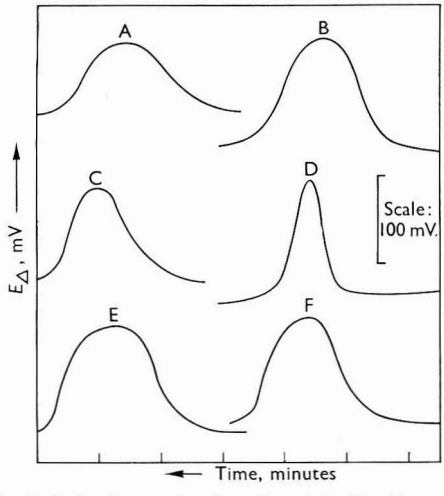


Fig. 3. Typical chart records of coulometric titrations of 1 ml of acid; curve A, for 0·01M acetic acid; curve B, for 0·01M perchloric acid; curve C, for 0·001 M acetic acid; curve D, for 0·001M perchloric acid; curve E, for 0·0001M acetic acid; curve F, for 0·0001M perchloric acid. Chart speed, 60 inches per hour

arms and connected to the differential electrolytic potentiometric circuit. Coulometric electrodes, either a working electrode and a capillary lock auxiliary electrode,[7,8] or, as shown, two working electrodes, are plugged into the top of the cell through a rubber bung. For determination of acids, the arrangement shown is used, consisting of a cathode of 1 inch of 22-s.w.g. platinum wire coiled into a spiral, and a similar anode of pure silver wire. A paddle, 10 mm long, of iron wire sealed into capillary tubing serves for stirring. The cell holds 1 to 2 ml of solution. The circuit of Fig. 1 is used with the appropriate single standard resistor for measuring the generating current.

Procedure—

The cell is flushed with oxygen, plugged and weighed. Calibrated Kirk pipettes, of capacity 50 to 1000 μl, are used to transfer the sample to the cell under a flow of oxygen, and the cell is re-plugged and re-weighed, so that the sample size is accurately known by weight. *Water* is added if necessary to cover the electrodes (2 ml), together with 60 mg of potassium bromide per ml of solution, and the determination conducted, at fractional milliamp generating currents, by method (*i*) described above. The differential electrodes are in place throughout, the complete titration is recorded and the calibrated chart drive is used for measuring time.

Results and discussion

Typical results are recorded in Table I, and sample chart records of the final stage of each type of titration are shown in Fig. 3. As little as 10^{-7} mole of strong or weak acid can be determined precisely and speedily, with plenty of reserve sensitivity. With highly diluted solutions residual carbon dioxide in the *water* used to dilute the cell contents to 2 ml is detectable, and its presence was corrected for by titrating 1 ml of 10^{-4} M acid (perchloric or acetic) and 1 ml of *water*, and then 2 ml of 10^{-4} M acid. The first result *minus* one half of the second approximates to the amount of carbon dioxide added in 1 ml of the *water*, and was subtracted in proportion to the amount of *water* added in subsequent determinations. The amount corresponded to 7×10^{-8} g of carbon dioxide per ml of *water*, a concentration of $1{\cdot}6 \times 10^{-6}$ M. Again extremely high differentiating current densities were used to produce wide end-point peaks, from which the true end-points were obtained by the method of Cailletet and Matthias. The increasing relative amount of residual carbon dioxide and the increasing tendency to overshoot as the stock acid is progressively diluted account for the increasing positive error, which could be considerably diminished by empirical calibration. Nevertheless, an accuracy of 2 per cent. for 10^{-7} mole of acetic acid in a 2-ml sample is considered acceptable.

Table I

Coulometric determinations on semi-micro scale

Nominal amount titrated	Differential current density, amp per sq. cm	Generating current, mA	Coulombs— measured	Coulombs— average, corrected for carbon dioxide	Coulombs— calculated	Error of mean, per cent.
Perchloric acid—						
1 ml 10^{-4} M	5×10^{-6}	0·1	0·0105, 0·0110, 0·0100, 0·0111, 0·0100, 0·0110	0·0103	0·0099	+4·0
2 ml 10^{-4} M	5×10^{-6}	0·1	0·0211, 0·0208, 0·0198, 0·0205	0·02055	0·0198	+4·0
1 ml 10^{-3} M	$7{\cdot}5 \times 10^{-6}$	0·5	0·1014, 0·1014, 0·1008, 0·1004	0·1007	0·0991	+1·6
1 ml 10^{-2} M	$1{\cdot}0 \times 10^{-6}$	0·5	0·9915, 0·9895	0·9902	0·9910	−0·08
Acetic acid—						
1 ml 10^{-4} M	5×10^{-6}	0·1	0·0108, 0·0107, 0·0103	0·0103	0·0101	+2·0
1 ml 10^{-3} M	$7{\cdot}5 \times 10^{-6}$	0·1	0·1018, 0·1018, 0·1012, 0·1011, 0·1006	0·1010	0·1007	+0·3
1 ml 10^{-2} M	1×10^{-6}	0·5	1·0070, 1·0070	1·0067	1·0071	−0·04

Other observations

Satisfactory results have been obtained for the anodic determination of bases, by using a capillary-lock auxiliary-cathode[7,8] layer charged with copper sulphate and sodium sulphate and a base electrolyte of sodium sulphate, but the subject has not been pursued.

To eliminate the troublesome preparation and handling of base solutions, attempts were made with the platinum - silver system in a bromide electrolyte to generate known amounts of hydroxyl ion for subsequent volumetric back-titration with standard acid delivered from a micrometer-syringe burette. A loss of current efficiency of as much as 40 per cent. resulted; after investigation, this was traced to the discharge of hydroxyl ions at the silver anode at the same time as the discharge of bromide ions. It became plain that generation of hydroxyl ions with this electrode system is not practicable in solutions of pH much greater than 7.

Attempts were also made to determine acids or bases in non-aqueous media. Glacial acetic acid, acetone and acetonitrile, under various conditions, failed to yield satisfactory results. Methanol alone gave acceptable results, but distortion of the peaks and sluggish electrode response detracted greatly from their usefulness.

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References

1. Bishop, E., and Short, G. D., *Analyst*, 1962, **87**, 467.
2. Short, G. D., and Bishop, E., *Ibid.*, 1962, **87**, 724.
3. ——, ——, *Ibid.*, 1962, **87**, 860.
4. Bishop, E., and Short, G. D., *Anal. Chem.*, 1964, **36**, 730.
5. Short, G. D., "Current - Potential Relationships at Antimony Electrodes," Ph.D. Thesis, University of Exeter, 1963.
6. Bishop, E., and Short, G. D., *Analyst*, 1964, **89**, 415.
7. Bishop, E., *Mikrochim. Acta*, 1960, 803.
8. Bishop, E., and Dhaneshwar, R. G., *Anal. Chem.*, 1964, **36**, 726.
9. Monk, R. G., and Steed, K. C., *Anal. Chim. Acta*, 1962, **26**, 305.
10. Bishop, E., and Dhaneshwar, R. G., *Analyst*, 1962, **87**, 845.
11. Lingane, J. J., "Electroanalytical Chemistry," Second Edition, Interscience Publishers Inc., New York and London, 1958, p. 607.
12. Delahay, P., *J. Electrochem. Soc.*, 1950, **97**, 198, 205.
13. Lingane, J. J., and Small, L. A., *Anal. Chem.*, 1949, **21**, 1119.
14. Carson, W. N., and Ko, R., *Ibid.*, 1951, **23**, 1019.
15. Bishop, E., and Dhaneshwar, R. G., *Analyst*, 1963, **88**, 424.
16. Bishop, E., and Short, G. D., *Talanta*, 1964, **11**, 393.
17. Reilley, C. N., Cooke, W. D., and Furman, N. H., *Anal. Chem.*, 1951, **23**, 1030.
18. Reilley, C. N., Adams, R. N., and Furman, N. H., *Ibid.*, 1952, **24**, 1044.
19. Ehlers, V. B., and Sease, J. W., *Ibid.*, 1954, **26**, 513.
20. Bishop, E., *Mikrochim. Acta*, 1956, 619.

NOTE—References **1**, **2**, **3**, 4, 6, 7, 8 and 10 are to Parts VI, VII, IX, XIII, XIV, IV, XII and VIII, respectively.

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The Analysis of Stainless-steel Neutron-activation Products by Combined Group Separation and γ-Ray Spectrometry

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An ion-exchange method is described for separating stainless-steel activation products into three groups before analysis by γ-ray spectrometry. The method was devised for samples from pressurised water loops containing mixtures of radioactive nuclides difficult to analyse by direct γ-ray spectrometry.

The radiochemical analysis of mixtures of neutron-activated stainless-steel corrosion products is an essential part of the study of the migration and deposition of these species in pressurised water loops.[1] The method reported here was devised for the radiochemical analysis of samples from an out-of-pile loop. In this experiment a strip of irradiated steel was placed in an autoclave in the loop, and measurements were required of the radioactivity in the strip compared with that deposited on metal discs both upstream and downstream from the strip, and that of the particulate matter filtered from the loop water by Millipore "crud" filters. Sufficient information could be acquired for the interpretation of the corrosion processes by determining the long-lived γ-ray emitting nuclides present in the samples; these could possibly include iron-59, cobalt-60 and -58, manganese-54, zinc-65, chromium-51, tantalum-182 and antimony-124. Although certain of these nuclides are produced in comparatively small amounts by neutron irradiation of steel, preferential migration can lead to their concentration to significant levels in some samples.

In favourable instances, samples containing mixtures of some of these nuclides may be analysed non-destructively by γ-ray spectrometry. Unfortunately this technique fails for mixtures of nuclides that have spectra with photopeaks of similar energy, since precision is then low and small energy-calibration errors cause gross inaccuracies, particularly for minor components.[2] For such samples alternative methods of analysis must be sought.

In view of the large number of samples to be handled, it was desirable to avoid complete chemical separation with subsequent radiometric analysis because this procedure is time-consuming. An attractive compromise between direct γ-ray spectrometry and complete separation is the separation of nuclides into groups in which they are amenable to γ-ray spectrometric analysis.[3,4,5,6]

The relative merits of separation schemes possibly applicable were considered. Though Samsahl[3] has devised an ion-exchange separation scheme specifically for the groupwise separation of neutron-activated stainless steel and its corrosion products, it has certain disadvantages. Firstly, iron-59 and cobalt-60 appear in the same group and consequently require further separation before radiometric analysis and secondly, the method is unsuitable for samples containing large amounts of iron such as our steel deposition disc samples (approximately 1 g of iron per disc). A development[4,5,6] of this scheme, though resolving the former difficulty, still suffers from the latter. Theoretically, the ion-exchange separation scheme, proposed by Headridge and Dixon[7] on the basis of equilibrium distribution coefficients, divides the nuclides into groups in which they may be determined by γ-ray spectrometry. If an eluent solution M in hydrofluoric acid and 0·1 M in hydrochloric acid is used, anionic fluorides including those of tantalum and antimony are absorbed on De-Acidite FF, cations including cobalt, zinc and manganese are absorbed on Zeo-Karb 225, and "neutral" fluorides including those of iron and chromium are not absorbed and appear in the effluent.

As Headridge and Dixon's[7] scheme appeared to be the most suitable, its application to the analysis of steel neutron-activation products by combined group separation and γ-ray spectrometry was investigated.

Method

Apparatus—

Plastic ware—Polythene and polystyrene apparatus was used throughout for handling all solutions containing hydrofluoric acid.

Polythene chromatographic columns were used (length 30 cm, internal diameter 0·9 cm).

Polystyrene weighing bottles (100 ml, 2-inch diameter × 2·125 inches) calibrated at 50 ml were used as standard counting vessels for resins. Polythene screw-top jars were used as counting vessels for the effluent.

Counting equipment—The γ-ray spectrometer used a 3 × 3-inch sodium iodide (thallium) scintillation detector with a 100-channel pulse-height analyser. Paralysis errors were eliminated by incorporating a live-time integrator.

Resins—

Zeo-Karb 225—Type SRC 14 with 8 per cent. cross-linking and a particle size of 52 to 100 mesh was used. Convert the resin from the sodium to the hydrogen form before use by treating it with 2 N hydrochloric acid and then washing it with water until free from chloride.

De-Acidite FF—Type SRA 70 with 7 to 9 per cent. cross-linking and a particle size of 52 to 100 mesh was used. Treat the resin with 2 N hydrochloric acid and then wash it with water.

Radioactive tracers—

Solutions of cobalt-60 and -58, manganese-54, zinc-65, iron-59, chromium-51, tantalum-182 and antimony-124 were obtained from the Radiochemical Centre, Amersham, or by irradiating Specpure specimens of the elements or their oxides in the Harwell reactor BEPO.

Reagents—

All the reagents should be of AnalaR or Specpure quality.

Eluent solution—Use a solution M in hydrofluoric acid and 0·1 M in hydrochloric acid.

Procedure—

Dissolve the deposition-disc samples *plus* 5 mg of tantalum and 5 mg of antimony oxide in a nitric acid - hydrofluoric acid mixture (1 + 3, by volume). Similarly treat "crud-filter" samples and add an inactive deposition disc to keep the composition of all sample solutions identical. Add a few drops of 100-volume hydrogen peroxide. Evaporate the solution twice to dryness with hydrofluoric acid and dissolve the residue in 50 ml of eluent. Pass the solution through a 10-ml column of De-Acidite FF and wash the column with 50 ml of eluent. Then pass the combined effluent and washings through a 10-ml column of Zeo-Karb 225 and wash the column with 125 ml of eluent. Maintain a flow-rate of 1 ml per minute throughout. Transfer the resins to standard counting vessels and dilute them with resin to 50 ml. Dilute the effluent to a standard volume in a screw-top polythene jar. Assay the activities of these fractions by γ-ray spectrometry at standard geometries.

Discussion and results

Decontamination factors—

To establish the best conditions for elution, preliminary tracer experiments were carried out; the decontamination factors of the resins and effluents for the elution conditions finally chosen and described in the procedure, are given in Table I.

With the exception of the elution of chromium from Zeo-Karb 225 the decontamination factors are adequate and confirm the predictions of Headridge and Dixon. Fortunately the separation technique is still useful because chromium-51 does not interfere with the γ-ray spectrometric determination of other nuclides in the Zeo-Karb 225 group, since it has no γ-ray contribution above an energy of about 0·4 MeV. For the procedure adopted, 98 per cent. of the chromium-51 was found in the effluent. Consequently, all chromium-51 count rates are corrected for this yield.

APPLICABILITY OF THE METHOD—

The method was tested by analysing several radioactive nuclide mixtures of known composition. The γ-ray spectra obtained were resolved mathematically from the counts found in the major photopeaks (see Table III). The results are shown in Table II.

TABLE I

RESIN AND EFFLUENT DECONTAMINATION FACTORS FOR THE ELUTION CONDITIONS FINALLY ADOPTED

	Decontamination factors			
	De-Acidite FF		Zeo-Karb 225	
Nuclide	Resin	Effluent	Resin	Effluent
Tantalum-182	Absorbed	3×10^3	2×10^3	Eluted
Antimony-124	Absorbed	10^3	10^3	Eluted
Cobalt-60	10^4	Eluted	Absorbed	6×10^3
Manganese-54	8×10^3	Eluted	Absorbed	10^4
Zinc-65	10^3	Eluted	Absorbed	10^4
Iron-59	10^4	Eluted	7×10^3	Eluted
Chromium-51	10^3	Eluted	50	Eluted

TABLE II

RESULTS FOR THE DETERMINATION OF MIXTURES OF STEEL-ACTIVATION PRODUCTS BY COMBINED GROUP SEPARATION AND γ-RAY SPECTROMETRY

Sample No.	Nuclide	^{182}Ta	^{124}Sb	^{60}Co	^{58}Co	^{65}Zn	^{54}Mn	^{59}Fe	^{51}Cr
1a	Taken (counts/min.)	15,934	—	8052	—	—	21,038	11,104	1404
	Found (counts/min.)	15,557	—	8312	—	—	21,110	10,956	1435
	Recovery, per cent.	97·6	—	103·2	—	—	100·3	98·7	102·2
1b	Taken (counts/min.)	16,570	—	8052	—	—	21,038	11,104	1404
	Found (counts/min.)	16,007	—	8135	—	—	21,343	11,087	1398
	Recovery, per cent.	96·6	—	101·0	—	—	101·5	99·8	99·6
2a	Taken (counts/min.)	8013	—	7992	—	9581	9983	4048	2079
	Found (counts/min.)	8150	—	8167	—	9591	10,319	3952	2056
	Recovery, per cent.	101·7	—	102·2	—	100·1	103·4	97·6	98·8
2b	Taken (counts/min.)	7945	—	7992	—	9581	9983	4048	2079
	Found (counts/min.)	8105	—	8097	—	9603	10,498	4028	2058
	Recovery, per cent.	102·0	—	101·3	—	100·2	105·2	99·5	98·9
3a	Taken (counts/min.)	5080	12,167	17,993	4447	5056	—	9084	—
	Found (counts/min.)	5204	12,247	18,127	4527	5325	—	9115	—
	Recovery, per cent.	102·4	100·7	100·7	101·8	105·3	—	100·3	—
3b	Taken (counts/min.)	5080	12,167	17,993	4447	5056	—	9084	—
	Found (counts/min.)	5267	12,268	18,170	4407	5164	—	9190	—
	Recovery, per cent.	103·7	100·8	101·0	99·1	102·1	—	101·2	—

The recoveries obtained for both major and minor components are similar to those that might be expected for complete chemical separation with subsequent radiometric assay, and are therefore highly satisfactory. Good counting statistics were ensured by counting for 10 minutes at high count rates to increase the probability that errors found were owing to deficiencies in the separation procedure.

If the separated groups are analysed by γ-ray spectrometry, the statistical error imposed on the amount of a nuclide found in a mixture is dependent both on the number of nuclides present and their relative abundances; consequently, it is only practicable to calculate such errors as each individual mixture of nuclides is encountered.

To illustrate the advantages of the combined method over direct γ-ray spectrometry when photopeak overlap occurs, the precisions and accuracies obtainable by both methods have been calculated on the basis of counting statistics for a mixture of iron-59 (10,000 counts), cobalt-60 (2500 counts), zinc-65 (10,000 counts) and tantalum-182 (2500 counts). The comparison is depicted diagrammatically (see Fig. 1). The photopeaks used in the mathematical resolution of the spectra of nuclide mixtures are given in Table III.

TABLE III

PHOTOPEAKS USED IN THE MATHEMATICAL RESOLUTION OF NUCLIDE MIXTURES

Nuclide	^{182}Ta	^{124}Sb	^{60}Co	^{58}Co	^{65}Zn	^{54}Mn	^{59}Fe	^{51}Cr
Photopeak	1·12	0·60	1·17	0·51*	0·51*	0·84	1·10	0·32
Energy, MeV ..	1·19	—	1·33	0·81	1·11	—	1·29	—
	1·22	—	—	—	—	—	—	—
	1·23	—	—	—	—	—	—	—

* Positron annihilation peak.

For the γ-ray spectrometer used, an energy misalignment of up to $\pm 0{\cdot}5$ channel was possible at 1·2 MeV for a channel width of 10 KeV, *i.e.*, a gain error of up to $\pm 0{\cdot}4$ per cent.

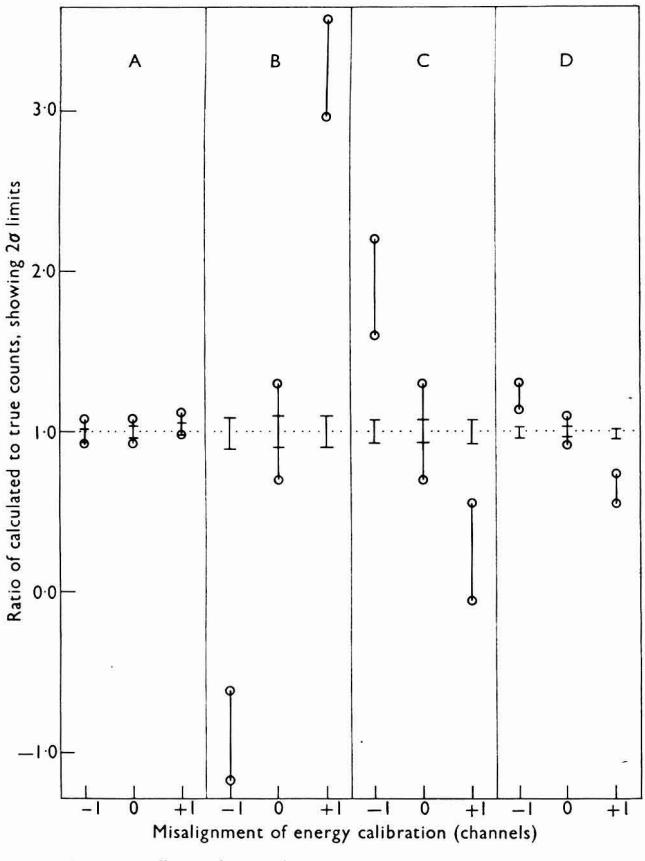

Fig. 1. Effect of misalignment of energy calibration on the analysis of the four-component mixture. Set A, zinc-65, 10,000 counts; set B, cobalt-60, 2500 counts; set C, tantalum-182, 2500 counts; set D, iron-59, 10,000 counts. o—o, 2σ limits for direct γ-ray spectrometry; I—I, 2σ limits for combined group separation and γ-ray spectrometry.

In these circumstances, the analysis of the sample nuclide mixture is obviously quite impossible by direct γ-ray spectrometry because of the probable large inaccuracies, particularly for the minor components, cobalt-60 and tantalum-182. The use of combined group separation and

γ-ray spectrometry produces the desired improvements in both precision and accuracy even with maximum energy misalignment. Although the accuracy of results obtainable by direct γ-ray spectrometry may be improved by servo-stabilisation of the γ-ray spectrometer gain,[8,9,10,11] its worth is questionable since the precision of the results remains inherently poor.

References

1. Walton, G. N., and Hesford, E., "The Migration of Activated Corrosion Products in High-pressure Water Loops." Conference on "Corrosion of Reactor Materials," International Atomic Energy Agency, Vienna, 1962.
2. Salmon, L., *U.K. Atomic Energy Research Establishment Memorandum* AERE-M 1140, Harwell, 1963.
3. Samsahl, K., *Acta Chem. Scand.*, 1958, **12**, 1292.
4. ——, *Aktiebolaget Atomenergi Report* AE-54, Stockholm, 1961.
5. ——, *Aktiebolaget Atomenergi Report* AE-56, Stockholm, 1961.
6. Samsahl, K., and Soremark, R., Proceedings of the International Conference on "Modern Trends in Activation Analysis," College Station, Texas, December, 1961, 149.
7. Headridge, J. B., and Dixon, E. J., *Analyst*, 1962, **87**, 32.
8. de Waard, H., *Nucleonics*, 1955, **13**, 36.
9. Scherbatskoy, S. A., *Rev. Sci. Instrum.*, 1961, **32**, 599.
10. Fite, L. E., Gibbons, D., and Wainerdi, R. E., Proceedings of the International Conference on "Modern Trends in Activation Analysis," College Station, Texas, December, 1961, 102.
11. Chase, R. L., *IRE* (*Inst. Radio Engrs.*), *Trans. Nucl. Sci.*, 1962, **9**, 119.

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The Determination of Uranium-235 by Neutron Activation and Ring-oven Separation of Molybdenum-99 - Technetium-99

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A method is described for determining uranium-235 in a uranium sample by a neutron-activation technique. The fission product, molybdenum-99 - technetium-99, is separated from the neutron-activated sample on a ring-oven, and is then determined by γ-ray spectrometry. The precision of the method is about 1 per cent. over the range 0·4 to 0·7 per cent of uranium-235.

A procedure that can be used for determining the uranium-235 isotopic content of uranium is based on the separation and measurement of a fission product formed by neutron activation of the sample. The relative activities of the selected fission product in the sample and in a uranium standard are then proportional to their uranium-235 contents.[1,2]

The ring-oven technique has been used for separating caesium-137 from irradiated uranium fuel.[3] The method involves the retention of the unwanted fission products in a carrier-free state on a ferric hydroxide precipitate situated at the centre of a filter-paper, and removal of the caesium-137 (containing added caesium carrier) to the ring zone.

A similar method was considered feasible for separating a fission product obtained from a brief neutron activation of uranium samples, but because of the extremely short radioactivation period only the shorter half-life fission products of high yield are of use for this determination. Molybdenum-99 - technetium-99*m* (half-life, 67 hours) was chosen for this work, because it is formed in high yield (6·1 per cent.) and also has a well established γ-ray spectrum, precursors that are extremely short-lived and non-volatile, and it readily forms anionic species in solution. Consequently, by adding molybdate carrier to a radio-activated solution of uranium, a ring-oven separation should be possible by retaining the carrier-free alkaline-earth, rare-earth and zirconium - niobium activities on a ferric hydroxide precipitate at the centre of a filter-paper, and washing the molybdenum-99 - technetium-99 to the ring zone with ammonia solution and water. Under these conditions ruthenium may move to the ring zone with the molybdenum - technetium if anionic species of ruthenium are formed. Examination of the γ-ray spectra of the possible ruthenium contaminants shows that whereas the γ-ray spectrum of ruthenium-103 - rhodium-103 has little in common with the γ-ray spectrum of molybdenum-99 - technetium-99*m*, ruthenium-105 - rhodium-105 has many similar γ-ray energies. However, since the latter has a half-life of only 4·5 hours, it can be allowed to decay substantially without seriously affecting the molybdenum-99 - technetium-99*m* measurement.

Experimental

Behaviour of molybdenum-99 - technetium-99—

A nominal 1-μl sample of molybdenum-99 - technetium-99 solution containing molybdate carrier was placed on a ferric hydroxide precipitate, 8 mm in diameter, at the centre of a Whatman No. 540 filter-paper. The paper was placed on a ring oven and washed once with ammonia solution and then with de-ionised water. After five washes to the ring zone, no activity remained on the ferric hydroxide precipitate.

Since it was intended to irradiate small volumes of highly concentrated uranium solutions for this analysis, the procedure was repeated with a solution containing 250 mg of uranium per ml in 4 N nitric acid that contained molybdenum-99 - technetium-99 with carrier. In this instance replicate separations showed that up to 20 per cent. of the activity remained on the ferric hydroxide precipitate after five washes. This effect was attributed to the mechanical retention of molybdate ions by the thick ammonium diuranate precipitate that is formed at the first washing with ammonia solution. By increasing the diameter of the

ferric hydroxide precipitate to 12 mm, and dispersing the uranium - molybdenum-99 - technetium-99 spot to within 2 mm of the edge of the precipitate by washing it with water before washing it with ammonia solution, over 99 per cent. of the activity was concentrated in the ring zone after five washes. The proportion of its total activity concentrated in the ring zone after each wash is given below—

Number of washes	1	2	3	4	5	8
Activity removed to ring zone, per cent. ..	84·5	97·9	98·9	99·0	99·3	99·2

Further, replicate separations showed that the removal of the activity to the ring zone was reproducible if five washes were made—

Sample number	1	2	3	4	5	6	7	8	Mean	Standard deviation
Molybdenum-99 - technetium-99 removed to ring zone, per cent.	99·3	98·5	99·0	99·8	99·4	99·3	99·8	99·2	99·3	0·41

BEHAVIOUR OF NEUTRON-ACTIVATED URANIUM—

A 70-mg sample of depleted uranium oxide was dissolved in 0·2 ml of 8 N nitric acid, sealed in a silica tube, and then irradiated for 2 hours in the Harwell pile, BEPO, in a thermal neutron flux of 10^{12} neutrons per sq. cm per second. After the radioactivity had been allowed to decay for 24 hours, the silica ampoule was opened and a few drops of an acidified ammonium molybdate solution were added. A 1-μl sample of the irradiated solution was then placed on a 12-mm diameter pre-formed ferric hydroxide precipitate at the centre of a Whatman No. 540 filter-paper. The paper was placed on a ring oven and washed with sufficient water to disperse the original spot to within 2 mm of the outer edge of the precipitate. It was then washed once to the ring zone with ammonia solution and four times with de-ionised water. Finally, the ferric hydroxide portion of the paper was removed and the ring zone examined by γ-ray spectrometry. This showed that besides the molybdenum-99-technetium-99*m* spectrum, the presence of ruthenium-103 could be identified by its photopeak at 0·5 MeV.

Since it was intended to use the technetium-99*m* photopeak at 0·14 MeV for the quantitative measurement of the molybdenum activity, a half-life determination was made by counting this peak at 6-hourly intervals. The sample was live-time counted by using a 400-channel γ-ray scintillation spectrometer in conjunction with a $1\frac{3}{4}$-inch diameter $\times$ 2-inch deep sodium iodide thallium-activated crystal. The background was stored in the analyser and automatically subtracted from each count throughout the decay measurement. The area under each photopeak was then measured and a decay curve plotted. A value of 66 hours was obtained, which confirmed that the technetium was in equilibrium with the molybdenum, and that the 0·14-MeV photopeak was free from any other γ-ray emitter of similar energy.

METHOD

REAGENTS—

Ferric chloride solution—Dissolve 2·4 g of hydrated ferric chloride, $FeCl_3.6H_2O$, in 100 ml of de-ionised water that contains 4 ml of concentrated hydrochloric acid, sp.gr. 1·18.

1 ml of solution $\equiv$ 5 mg of iron^{III}.

Ammonia solution, sp.gr. 0·88.

Nitric acid, diluted—Dilute concentrated nitric acid, sp.gr. 1·42, with an equal volume of water.

Ammonium molybdate solution—Dissolve 3·7 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 100 ml of de-ionised water. Acidify 10 ml of this solution with 0·1 ml of nitric acid, sp.gr. 1·42, immediately before use.

1 ml of solution $\equiv$ 20 mg of molybdenum.

SAMPLE PREPARATION AND IRRADIATION—

Prepare an irradiation ampoule by sealing one end of an 8- to 10-cm length of nominally 0·6-cm outer diameter, 0·4-cm inner diameter silica tubing. Fire in a calibration mark about 3 cm from the sealed end of the tube, and then clean the tube thoroughly and dry it. This mark, which represents about 0·3 ml, permits the tube to be used as a calibrated micro flask after the irradiation.

Accurately weigh approximately 70 mg of the purified dried sample in the form of U_3O_8 into the tube and add 0·2 ml of diluted nitric acid. Draw out the open end of the tube about 6 cm from the sealed end, and place in an ice-bath. After the tube has cooled, seal off the neck and place the ampoule in an oven at 100° C for 24 hours. This serves the dual purpose of dissolving the uranium oxide and effects the required pressure safety test before irradiation. Pack the ampoule in cotton wool in a standard 3-inch aluminium can and irradiate it for 2 hours in a neutron flux of 10^{12} neutrons per sq. cm per second. Set the can aside behind lead shielding for about 24 hours to allow its radioactivity to decay and then cut off the top of the ampoule (see Appendix). By using a capillary tube, transfer any solution and washings from the top of the ampoule into the bulk of the solution, and then add a few drops of molybdate solution, sufficient to give a final concentration of 5 mg of molybdenum per ml of solution. Dilute the solution to the mark with de-ionised water. Carefully mix the solution by placing a drawn-out glass tube into it, and then pulsing the solution up and down by pressing and releasing a rubber teat over the end of the tube. On no account bubble air into the ampoule otherwise serious losses of the solution may occur. Treat both sample and standard identically throughout.

RING-OVEN SEPARATION—

Prepare a ferric hydroxide precipitate on a Whatman No. 540 filter-paper by adding ammonia solution to a 12-mm spot of ferric chloride solution placed at the centre of the paper. By using a capillary micropipette, place 1 μl of the irradiated sample on the precipitate and carefully disperse the sample to within 2 mm of the edge of the precipitate with water. Wash to the ring zone once with ammonia solution and a further four times with water. Allow the paper to dry and then cut away the ferric hydroxide portion. Mount the ring zone on a flat aluminium counting disc, cover it with an aluminium absorber weighing about 500 mg per sq. cm and accurately position it in the detector chamber of a γ-ray scintillation spectrometer. Allow at least 30,000 counts to accumulate under the 0·14-MeV technetium-99*m* photopeak and then immediately count a standard that has been treated identically to the sample. Measure the 0·14-MeV photopeak areas for both standard and sample and correct them for dead-time and background if this has not been achieved automatically by the spectrometer. Finally calibrate the irradiation ampoules.

CALCULATION OF RESULTS—

Calculate the activity in the sample and standard by relating the corrected count rate with the initial weight of sample and the final calibrated volume of the irradiation ampoule. Then—

$$\frac{\text{Count rate of sample (counts per second per mg)}}{\text{Count rate of standard (counts per second per mg)}} = \frac{\text{uranium-235 content of sample}}{\text{uranium-235 content of standard}}$$

Hence, by using a natural uranium standard—

$$\text{Uranium-235 in sample, per cent.} = \frac{0{\cdot}715 \times \text{count rate of sample (counts per second per mg)}}{\text{count rate of standard (counts per second per mg)}}$$

RESULTS

The precision of the method was determined by replicate analyses on a sample of depleted uranium oxide. The results (see Table I) show that a precision of 1 per cent. is attainable

TABLE I

PRECISION OF METHOD WITH DEPLETED U_3O_8

Uranium-235, *determined by mass spectrometry*—
Per cent. uranium-235 .. .. 0·428 ± 0·002

Uranium-235, *determined by proposed method*—

Sample	1	2	3	4	5	6	7	8	9
Per cent. uranium-235	0·428	0·421	0·426	0·418	0·425	0·428	0·432	0·427	0·419

Mean = 0·425. Standard deviation = 0·0047. Coefficient of variation = 1·1 per cent.

and that comparison with the results obtained by an independent laboratory using a mass-spectrometer technique is excellent.

In addition, mixtures of this depleted sample and natural uranium oxide were prepared by accurate weighing and careful mixing, and then analysed by the proposed method. Excellent agreement was obtained between the calculated and determined results over the range 0·4 to 0·7 per cent. of uranium-235 (see Table II).

TABLE II

RESULTS FROM MIXTURES OF DEPLETED AND NATURAL U_3O_8

The depleted U_3O_8 contained 0·428 per cent. of uranium-235 and natural U_3O_8, 0·715 per cent. of uranium-235

	Uranium-235, per cent.—	
Mixture	calculated	found by proposed method*
1	0·476	0·476
2	0·572	0·565
3	0·667	0·664

* Each figure is the mean of four separate results.

CONCLUSIONS

A satisfactory ring-oven method has been described whereby the uranium-235 isotopic content in depleted natural uranium is determined by measurement of molybdenum-99 - technetium-99*m* after radioactivation. The method is simple and the ring-oven separation can be completed within 5 minutes. Transference losses are minimised since the irradiation ampoule into which the sample is weighed is also used as a calibrated micro flask. The method is capable of a precision of 1 per cent. over the range 0·4 to 0·7 per cent. of uranium-235, and it is reasonable to assume that a similar precision should be obtainable over a wider range of uranium-235 contents than used for this work.

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Appendix

A METHOD FOR OPENING IRRADIATED SILICA AMPOULES

Irradiated silica ampoules are usually opened by crushing them in a suitable beaker. An improvement on this method has been described[4] whereby the ampoule is crushed in a vertical length of flexible plastic tube held over a beaker. For this determination it was necessary to open the irradiated ampoule without losses and then use it as a calibrated micro flask. The irradiated ampoule was cooled in ice to reduce the gas pressure and then placed upright in a 5-cm deep hole in a lead block, in which it fitted closely. A cut was made with a glass-knife where the ampoule emerged from the block, and then the top (about 1 cm) was cleanly broken off by using the correct size cork borer placed over the ampoule. Preliminary experiments with caesium-137 solutions sealed in silica showed that losses were negligible with this method, and no difficulties were observed throughout the development of the method described in this paper.

REFERENCES

1. Seyfang, A. P., and Smales, A. A., *Analyst*, 1953, **78**, 394.
2. Seyfang, A. P., *Ibid.*, 1955, **80**, 74.
3. Hilton, D. A., and Reed, D., *Ibid.*, 1964, **89**, 134.
4. Porritt, R., and Thackray, M., *Anal. Chem.*, 1963, **35**, 1111.

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A Thermogravimetric Study of the Mandelates of Zirconium and Hafnium

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The thermal decomposition of zirconium mandelate and hafnium mandelate was studied by using a Stanton recording thermobalance, with the object of assessing the use of these compounds for determining the two elements in admixture. It was concluded that their use cannot be recommended since the weight of the mandelate is greater than the stoicheiometric requirement.

Mandelic acid was first recommended as an extremely selective reagent for determining zirconium by Kumins,[1] who showed that the precipitate was zirconium tetramandelate, $Zr(C_6H_5.CH(OH).COO)_4$. He did, however, recommend that the analysis be completed by igniting the precipitate to the dioxide, ZrO_2. Further work by Hahn[2] showed that the precipitation of zirconium was quantitative from hydrochloric acid solution over a wide range of acidity (0·1 to 8 N), and also that the precipitation of hafnium was similarly quantitative.

The selectivity of mandelic acid for zirconium was attributed by Feigl[3] to the glycollic acid group, –CH(OH).COOH, which, by forming an inner complex with the metal atom, produces a stable compound in acid solution. Feigl further suggested that better reagents for zirconium might be developed by increasing the weighting effect either by substituting a naphthyl group for the phenyl group in mandelic acid or by substitution in the benzene ring.

These suggestions were investigated by Oesper and Klingenberg,[4] who concluded that both *p*-chloromandelic acid and *p*-bromomandelic acid showed great promise of being superior to the parent acid. They also formed the opinion that the direct weighing of zirconium mandelate was not possible because of the appreciable solubility of the salt and the difficulty of removing excess of reagent.

On these latter points, Kumins had recommended washing the salt with a 5 per cent. solution of mandelic acid in 2 per cent. hydrochloric acid. In a paper by Astanina and Ostroumov, describing an improved method, it was claimed that if Kumins' procedure was followed, and the salt subsequently washed with 95 per cent. ethanol to remove the excess of reagent, then direct weighing of zirconium mandelate gave results as good as those obtained by ignition to the dioxide.

As the result of a major investigation into the application of mandelic acid and many of its substituted compounds, Belcher, Sykes and Tatlow[6] established the facts below—

(*i*) The solubility of zirconium mandelate in water was 0·1560 g per litre.
(*ii*) Washing the precipitate with water only, gave low results both on direct weighing and on ignition.
(*iii*) Washing the precipitate as recommended by Kumins, gave high results by direct weighing, but correct results after ignition.
(*iv*) Washing the precipitate with a saturated solution of zirconium mandelate gave results that were slightly low, but consistent, by direct weighing.

In view of these conflicting results, Hahn and Baginski[7] concluded that the inaccuracies incurred by direct weighing were due to the formation of some basic salt, and consequently they examined the conditions of precipitation. They concluded that, provided certain conditions were observed, direct weighing was possible. These conditions were that the acidity of the solution should be at least 5 N in hydrochloric acid, and that the reagent should be added dropwise to the hot solution (85° to 95° C). Further, filtration should take place after the solution had been cooled, and the precipitate should be washed successively with saturated zirconium mandelate solution, 95 per cent. ethanol and diethyl ether.

The thermal decomposition of zirconium mandelate was reported by Stachtchenko and Duval,[8] the compound having been prepared by Kumins' method. They found that the composition of the precipitate agreed closely with that of the formula $Zr(C_6H_5.CH(OH).COO)_4$, and that it was stable up to 188° C. After rapid decomposition

the weight was a minimum at 700° C, after which it rose slowly to become constant at 959° C, (the oxide level). This last phenomenon was attributed to a partial reduction of zirconia by carbon after decomposition of the mandelate radical, followed by slow re-oxidation.

Similar behaviour was obtained by Dautel and Duval[9] for the thermal behaviour of hafnium mandelate. Decomposition in this instance began at 240° C and the oxide level was reached at 497° C, although again there was evidence of some reduction of the hafnia, followed by re-oxidation.

This survey shows some confusion, in that some authors claim that the direct weighing of zirconium mandelate gives accurate results, while other claim that the results are low, possibly owing to the formation of a basic salt. There is, however, no reference to the source of zirconium used in these investigations, particularly with regard to its hafnium content.

Experimental

The precipitates were prepared from solutions of pure zirconyl chloride and pure hafnyl chloride. Spectrographic analysis of these salts showed that they contained 0·0035 per cent. of hafnium (as HfO_2) and 0·91 per cent. of zirconium (as ZrO_2), respectively.

The method of Astanina and Ostroumov[5] was followed for preparing the individual mandelates of zirconium and hafnium, whereas the mixed mandelates were precipitated by using a modified procedure after consideration of the findings of Hahn and Baginski.[7] The thermogravimetric procedure was as described in a previous paper[10] on the thermal decomposition of the selenites of these metals.

Thermogravimetric procedure—

The thermogravimetric examination was made by using a Stanton recording thermobalance with a sensitivity of $\pm 0{\cdot}1$ mg.

The heating rate was linear and approximately 6·7° C per minute. The furnace was vertical and closed at the top; thus the precipitate was heated in air under static conditions.

The precipitate was contained in an 8-ml porous porcelain crucible (Berlin OO/A1). An upper limit of 1200° C was imposed to prevent any possible deterioration of the glaze.

In order to determine the buoyancy effect, each empty crucible was heated over the range to be used, and its weight was continuously recorded. The loaded crucible was similarly treated and the net weight at any given temperature was obtained as the difference between the gross weight and the tare weight.

It is from these derived results that the weight - temperature graphs were drawn.

Method

Procedure (*a*)—

Transfer by pipette 25 ml of the stock solution of either zirconyl chloride or hafnyl chloride, each in N hydrochloric acid, to a 250-ml beaker. Add 5 ml of 12 N hydrochloric acid and 20 ml of water to give an acidity of 1·7 N. Precipitate the zirconium or hafnium mandelate by adding 50 ml of a cold, saturated solution of mandelic acid (approximately 16 per cent. w/v) that has been freshly filtered. Raise the temperature of the solution to approximately 80° C and digest the solution for 20 to 30 minutes; it was found that longer periods of digestion make the precipitate less tractable.

Allow the precipitate to settle and decant the supernatant liquid through a porous porcelain crucible, leaving the bulk of the precipitate in the beaker. Wash the precipitate with a solution containing 5 per cent. mandelic acid in 1 per cent. hydrochloric acid, and decant the washings into the crucible. Repeat the washing procedure until all the precipitate is transferred to the crucible, and then wash it with 95 per cent. ethanol.

Wipe the outside of the crucible and place it in a desiccator overnight before examination in the thermobalance.

Procedure (*b*)—

Transfer by pipette, 25 ml of the stock solution of mixed zirconyl and hafnyl chlorides in N hydrochloric acid to a 250-ml beaker. Add 18·75 ml of 12 N hydrochloric acid and 6·25 ml of water to give an acidity of 5 N. Raise the temperature of the solution to approximately 85° C. Carry out the precipitation, digestion, filtration and washing as in Procedure (*a*).

The precipitate obtained by this modified procedure is easier to handle, and filtration and washing can be accomplished in about 15 minutes compared with roughly 1 hour required for Procedure (*a*).

Results

Figs. 1 and 2 show typical decomposition curves of the mandelates of zirconium and hafnium, from which the facts below were deduced.

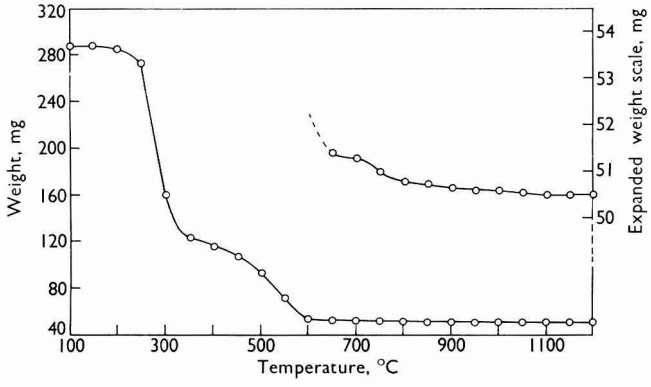

Fig. 1. Typical decomposition curve for zirconium mandelate

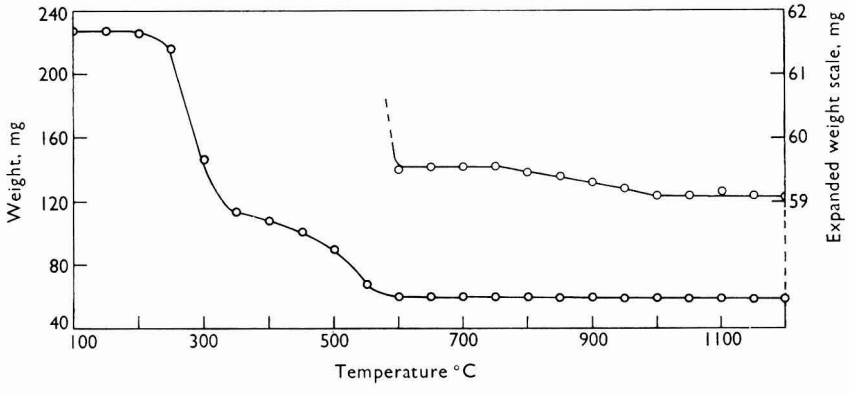

Fig. 2. Typical decomposition curve for hafnium mandelate

Zirconium mandelate—

The weight was constant up to 150° C and between this temperature and 200° C there was a small loss of some 2 mg from a sample of 300 mg. Above 200° C the decomposition became rapid, but at about 350° C the rate of loss of weight lessened giving an ill-defined step in the curve. At 500° C this rate increased again until at 600° C it abruptly became almost zero. There was then a further gradual loss of 2 mg up to 1000° C at which temperature constant weight was attained (see Fig. 1).

The molecular weight of the precipitates, calculated from the weight of zirconia after ignition, shows that the precipitate was heavier than the stoicheiometric requirement, as shown below—

Weight of precipitate, mg	Weight of ZrO_2, mg	Calculated molecular weight	Theoretical molecular weight
295·8, 287·3	51·1, 50·5	713·1, 701·0	695·8

HAFNIUM MANDELATE—

The decomposition curve (see Fig. 2) was similar to that for zirconium mandelate, although the small loss up to 200° C was less marked. The final small loss between 600° C and 1000° C was also less, amounting to approximately 1 mg.

The calculated molecular weight of the precipitates also was higher than required by stoicheiometry, as shown below—

Weight of precipitate, mg	Weight of HfO_2, mg	Calculated molecular weight	Theoretical molecular weight
228·7, 226·9	60·1, 59·2	797·0, 803·1	783·1

The calculated molecular weight was corrected for 1 per cent. of zirconia in the hafnia residue.

MIXED ZIRCONIUM AND HAFNIUM MANDELATES—

As might be expected, the decomposition curve for the mixed mandelates was similar to those for the individual compounds. Calculation of the percentages of hafnia in the mixture gives a low result, and this can be attributed directly to the fact that the precipitates are heavier than the theoretical weight as shown below—

Weight of mixed mandelates, mg	Weight of mixed oxides, mg	HfO_2 found, per cent.	HfO_2 actual, per cent.
261·4, 263·5	54·4, 55·3	43·64, 45·02	53·5

DISCUSSION

The results show that in every instance the weight of the precipitate is greater than the theoretical requirement, calculated from the weight of the oxide left after ignition. This error is not constant, and leads to the conclusion that it is due to an excess of mandelic acid that is not removed by washing. This also explains the low result obtained for the hafnia content of the mixed oxides since the ratio of hafnium mandelate to hafnia (3·720 to 1) is less than that of zirconium mandelate to zirconia (5·647 to 1).

The conclusions reached by Duval and his co-workers[8,9] that the precipitates agree well with the formula $M(C_6H_5.CH(OH).COO)_4$ can be attributed to the fact that they failed to detect the small loss in weight between 600° C and 1000° C, thus giving them a higher weight of oxide. It is also possible that the increase of weight that they recorded between these temperatures was due, not to re-oxidation of a partially reduced oxide, but to the buoyancy effect.

TABLE I

RE-CALCULATED RESULTS FOR ZIRCONIUM AND HAFNIUM MANDELATES

	Weight of mandelate, mg	Weight of oxide, mg		Calculated molecular weight		Theoretical molecular weight
		750° C	1100° C	750° C	1100° C	
Zirconium	295·8	52·0	51·1	700·9	713·1	695·8
	287·3	51·5	50·5	687·4	701·0	
Hafnium	228·7	61·0	60·1	789·2	801·0	783·1
	226·9	60·1	59·2	794·7	806·7	

TABLE II

CALCULATED HAFNIA CONTENT OF OXIDE RESIDUE

Weight of zirconium mandelate,* mg	Weight of oxide residue,* mg	Hafnia content calculated,† per cent.
361·8	64·9	3·68
611·5	109·5	3·27
490·6	87·8	3·07
248·7	44·5	3·03

* These figures are extracted from the paper of Belcher Sykes and Tatlow[6].

† These results for the hafnia content are consistent with what might be expected from material prepared from, say, the Travancore deposits.

These suggestions are supported if the assumption is made that the oxide level is reached at, say, 750° C. If the results quoted for zirconium and hafnium mandelate are re-calculated on this basis, then a much more favourable agreement is obtained (see Table I).

Belcher, Sykes and Tatlow[6] obtained precipitates of zirconium mandelate that weighed less than the stoicheiometric requirements. From this they concluded that some basic salt was being co-precipitated. There is, however, no indication of the source of zirconium used and it seems justifiable to assume that it was the normal commercially available material containing an amount of hafnium. If this is so, then the approximate hafnium content can be calculated (see Table II).

Conclusions

Generally one can conclude that the direct weighing of zirconium mandelate or hafnium mandelate can only be justified provided that an excess of mandelic acid can be completely removed by washing. This might possibly be achieved by extra care when the precipitate is washed with alcohol, but unfortunately alcohol renders the precipitate sticky and this makes filtration slow. If the final washings could be tested for mandelic acid, then the method would be improved. These conclusions agree with those expressed by Belcher and Wilson[11] in their appraisal of the use of this reagent for zirconium.

References

1. Kumins, C. A., *Anal. Chem.*, 1947, **19**, 376.
2. Hahn, R. B., *Ibid.*, 1949, **21**, 1579.
3. Feigl, F., "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press Inc., New York, 1949, p. 213.
4. Oesper, R. E., and Klingenberg, J. J., *Anal. Chem.*, 1949, **21**, 1509.
5. Astanina, A. A., and Ostroumov, E. A., *Zhur. Anal. Khim.*, 1951, **6**, 27; *Chem. Abstr.*, 1951, **45**, 6121*i*.
6. Belcher, R., Sykes, A., and Tatlow, J. C., *Anal. Chim. Acta*, 1954, **10**, 34.
7. Hahn, R. B., and Baginski, E. S., *Ibid.*, 1956, **14**, 45.
8. Stachtchenko, J., and Duval, C., *Ibid.*, 1951, **5**, 410.
9. Dautel, A., and Duval, C., *Ibid.*, 1959, **20**, 154.
10. Adams, R. W., and Holness, H., *Analyst*, 1964, **89**, 31.
11. Belcher, R., and Wilson, C. L., "New Methods in Analytical Chemistry," Chapman & Hall Ltd., London, 1955, p. 119.

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Constant-potential Amperometric Technique for the Successive Complexometric Determination of Calcium and Magnesium

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A direct method is described for the successive determination of both calcium and magnesium in the same sample by titration with EDTA. The technique of constant-potential amperometry is used with a combination of a platinum electrode and a silver amalgam electrode, and has advantages over potentiometric methods. A marked reduction in the current occurs at the end-point, and the accuracy and stability of the end-point are increased. This technique also permits the determination of calcium and magnesium in the presence of phosphate and citrate.

The value of the EDTA titre at pH 11·75, at a constant applied potential of 130 mV, represents the calcium content, and the titre at pH 9·60, at a constant applied potential of 210 mV, represents the total calcium and magnesium content.

Good recoveries are obtained by the proposed method.

The analytical applications of EDTA have been wide and varied and, in particular, its use for determining calcium and magnesium in the same solution has considerable advantages over older methods.[1] The direct methods of analysis for these constituents, *i.e.*, by titration with EDTA, have all permitted the determination of calcium and magnesium separately,[2,3] but in certain instances, *e.g.*, milk, where the ratio of calcium to magnesium is 10 to 1, this method is not desirable, since it is likely that a disproportionate error in magnesium values will be introduced.[4] A potentiometric method in which an automatic titrimeter is used[5] has been developed for determining calcium and magnesium in the same sample of water with EDTA, but this method did not lend itself satisfactorily to manual operation owing to the difficulty in critically differentiating the end-point. Since amperometric titrations have great advantages over potentiometric titrations,[6] a method involving the use of constant-potential amperometry[7] has been developed for the successive determination of calcium and magnesium in the same sample by direct titration with EDTA.

Experimental

Potentials varying from 80 to 350 mV were applied to the electrodes during each determination of calcium and magnesium, and the optimum values at which to make the determinations were found to be 130 mV for calcium and 210 mV for magnesium, since apart from a large fall in current at the end-point and at the correct pH values,[6] the maximum meter deflections were within the 6-inch scale of the 0 to 50-μA micro-ammeter used. The optimum potentials were applied to a combination of a platinum electrode and a silver amalgam electrode through a fully stabilised, variable-voltage a.c. source capable of supplying a constant potential.[8] The potentials across the electrodes and the pH of the solutions were all measured with a Polymetron type 42B precision pH meter.

Gaugin and Charlot[9] and Duyckaerts[10] have pointed out that in amperometry at constant potential a reversible system gives a curve of current *versus* millilitres of reagent rising to a rounded maximum at the midpoint, followed by a fall almost linear near the end-point, followed by a sharp rise if a reversible system is present beyond the end-point, or almost zero current if there is no process reversible at both electrodes. These observations were confirmed in our experiments and a typical curve obtained during the titration of one of the samples is shown in Fig. 1. A transistorised titrimeter[11] was used to measure the change in current.

METHOD

REAGENTS—

Sodium hydroxide, 0·1 N.
Hydrochloric acid, N.
Ammonia solution, N.

EDTA stock solution—A portion (37·225 g) of EDTA (disodium salt, dihydrate) was dissolved in water and the solution diluted to 1 litre with water.

EDTA, 0·02 M—A 200-ml portion of the EDTA stock solution was taken and diluted to 1 litre with water. The pH of this solution was about 4·60.

Mercuric nitrate, 0·004 M—A portion (1·38 g) of mercuric nitrate monohydrate was dissolved in water and sufficient nitric acid was added to the solution to make it clear. The clear solution was then diluted to 1 litre with water.

Complex salt solution—This solution was prepared to simulate milk serum by the method of Marier and Boulet.[12] Each 100 ml of solution contained 147·8 mg of calcium, 35·3 mg of magnesium, 234·7 mg of sodium citrate dihydrate and 175·0 mg of potassium orthophosphate.

Complex salt solution, diluted—One millilitre of 10 per cent. acetic acid and 1 ml of N sodium acetate solution[13] were added to 10 ml of the complex salt solution. The solution was then diluted to 100 ml with water. The pH of this solution was about 4·60.

PROCEDURE—

A portion (10 ml) of the diluted complex salt solution was placed in a beaker and 10 ml of water (double distilled in glass) added to the beaker. The pH of the solution was adjusted to 11·75 by adding the requisite amount of 0·1 N sodium hydroxide and by using a pH meter to measure the pH of the solution accurately. It was usually found that 20 ml of 0·1 N sodium hydroxide were sufficient to bring the pH of the solution to 11·75. About 0·2 ml of 0·004 M mercuric nitrate was then added to the solution; this increases the sensitivity of the end-point.[5] The beaker was then placed in a jacket through which water at 37 $\pm$ 0·01° C was passed. The beaker along with the jacket was placed on a magnetic stirrer and the electrodes placed in the solution. The silver amalgam electrode (positive) and the platinum electrode (negative) were connected to the terminals of a transistorised titrimeter.[11] A constant potential of 130 mV was applied to the electrodes; this potential was checked on the millivolt scale of the pH meter.

The solution was titrated with 0·02 M EDTA, delivered from a 5-ml microburette, until the current as indicated on the ammeter showed a sudden and steep fall. The titre at this point represented the calcium content of the solution.

The pH of the solution was then adjusted to 9·60 by adding N hydrochloric acid and N ammonium hydroxide and by using a pH meter to measure the pH accurately. It was usually found that 5 ml of N hydrochloric acid and 10 ml of N ammonium hydroxide were needed to bring the pH of the solution to 9·60.

The potential applied to the electrodes was raised to 210 mV and the value checked by using the millivolt scale of the pH meter. The titration was continued until there was again a steep and sudden fall in the current, indicating that the end-point had been reached. The total titre at this point represented the total calcium and magnesium content.

CALCULATION—

If a is the titre at pH 11·75 and b is the total titre at pH 11·75 and 9·60 then—

$$\text{Calcium content} = 0{\cdot}7611a$$
$$\text{and magnesium content} = 0{\cdot}4596(b - a).$$

These calculations were made on the basis that—

$$1 \text{ ml of EDTA solution} \equiv 0{\cdot}7611 \text{ mg of calcium.}$$
$$\equiv 0{\cdot}4596 \text{ mg of magnesium.}$$

The value for calcium was determined by using the permanganate method and that for magnesium by using the phosphate method.[14] The determinations were made with pure solutions of calcium and magnesium.

RESULTS

The proposed method was used for determining calcium and magnesium in pure solutions of (*a*) calcium chloride, (*b*) magnesium chloride, (*c*) a mixture of calcium and magnesium chlorides, and (*d*) a mixture of calcium and magnesium chlorides and citric and phosphoric acids. Recovery results are shown in Table I.

TABLE I

RECOVERY OF CALCIUM AND MAGNESIUM FROM PURE SOLUTIONS

Test solution	Calcium, mg per 100 ml added	Calcium, mg per 100 ml found	Recovery, per cent.	Magnesium, mg per 100 ml added	Magnesium, mg per 100 ml found	Recovery, per cent.
Calcium chloride	166·5	168·7	101·3	—	—	—
Magnesium chloride	—	—	—	12·00	11·89	99·1
Calcium chloride *plus* magnesium chloride	166·5	168·7	101·3	12·00	11·89	99·1
Calcium chloride *plus* magnesium chloride *plus* 177·4 mg of citric acid and 31·02 mg of phosphoric acid per 100 ml of solution ..	166·5	168·7	101·3	12·00	11·89	99·1

Recovery tests were also carried out on the complex salt solution with additions of (*a*) calcium, (*b*) magnesium, (*c*) calcium and magnesium, and (*d*) calcium and magnesium and citric and phosphoric acids. The results are shown in Table II.

TABLE II

RECOVERY OF CALCIUM AND MAGNESIUM FROM A COMPLEX SALT SOLUTION

Test solution	Calcium, mg per 100 ml added	Calcium, mg per 100 ml found	Recovery, per cent.	Magnesium, mg per 100 ml added	Magnesium, mg per 100 ml found	Recovery, per cent.
Complex salt solution	147·8	147·9	100·1	35·30	35·40	100·3
Complex salt solution *plus* 139·2 mg of calcium per 100 ml of solution	287·0	288·0	100·4	35·30	35·40	100·3
Complex salt solution *plus* 11·55 mg of magnesium per 100 ml of solution	147·8	147·9	100·1	46·85	46·89	100·1
Complex salt solution *plus* 138·9 mg of calcium, 11·54 mg of magnesium, 145·3 mg of citric acid and 30·44 mg of phosphoric acid per 100 ml of solution	286·7	285·7	99·7	46·84	46·89	100·1

The calcium and magnesium contents of several samples of water used at this Station were determined by using the proposed method and a method involving the use of EDTA with an indicator.[15] A comparison of the results obtained is shown in Table III.

TABLE III

COMPARISON OF RESULTS OF DETERMINATION OF CALCIUM AND MAGNESIUM IN SAMPLES OF WATER

Sample	Calcium, p.p.m. found by using— EDTA - indicator method	Calcium, p.p.m. found by using— EDTA - amperometric method	Magnesium, p.p.m. found by using— EDTA - indicator method	Magnesium, p.p.m. found by using— EDTA - amperometric method
Raw water— (open well)				
A	239	236	70	65
B	210	208	76	79
C	225	227	65	67
Softened water— (used in dairy)				
A	32	33	20	20
B	38	35	18	18
C	35	33	18	20
Blow-down water— (from boilers)				
A	15	13	12	13

Discussion

The proposed method is simpler, more accurate, quicker and more sensitive than potentiometric methods and also helps in distinguishing the end-points at the respective pH values more effectively. A typical curve of current *versus* volume of titrant added is shown in Fig. 1 and shows that large peaks of about 20 μA were obtained for calcium and magnesium at the respective pH values. A platinum electrode was used instead of a calomel electrode because, apart from being a "clean" electrode,[16] it gave a large break in the end-point at the proper pH value in the EDTA titration.[6]

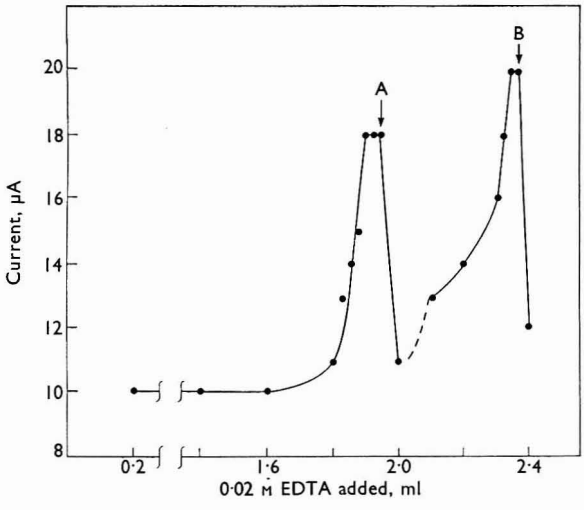

Fig. 1. Graph of current *versus* volume of EDTA used in the determination of calcium and magnesium. Titration carried out at pH 11·7 to calcium end-point A, and at pH 9·6 to magnesium end-point B

The values for calcium and magnesium found by the proposed method agree closely with the theoretical values (see Tables I and II). In colorimetric, spectrophotometric and titrimetric determinations in which certain indicators such as Eriochrome black T are used, the determinations for calcium and magnesium are usually carried out separately because of interference by phosphate. The proposed technique permitted the separate and successive determination of calcium and magnesium in the same sample without the need to eliminate phosphate. The recovery tests for calcium and magnesium in the presence of added phosphate showed that these two elements were fully accounted for and that the phosphate did not interfere. Previous workers on the determination of calcium by EDTA - indicator methods[17,18,19] have also shown that phosphate did not interfere in these determinations and the present determination by amperometric techniques confirmed their finding. The effect of adding citrate and a mixture of citrate and phosphate indicated that these two radicals had no effect on the determination (see Table II).

We thank the Director of Dairy Research, National Dairy Research Institute, Karnal, for his keen interest in this work.

References

1. Gehrke, C. W., *J. Ass. Off. Agric. Chem.*, 1962, **45**, 1.
2. Ling, E. R., *Analyst*, 1958, **83**, 179.
3. Jenness, R., *Anal. Chem.*, 1953, **25**, 966.
4. Davies, D. T., and White, J. C. D., *J. Dairy Res.*, 1962, **29**, 285.
5. Haslam, J., Squirrell, D. C. M., and Blackwell, I. G., *Analyst*, 1960, **85**, 27.
6. Kolthoff, I. M., *Anal. Chem.*, 1954, **26**, 1685.
7. Furman, N. H., *Ibid.*, 1954, **26**, 84.
8. Lewis, D. T., *Analyst*, 1961, **86**, 494.

9. Gauguin, R., and Charlot, G., *Anal. Chim. Acta*, 1953, **8**, 65.
10. Duyckaerts, G., *Ibid.*, 1951, **5**, 233.
11. Stock, J. T., *Analyst*, 1958, **83**, 56.
12. Marier, J. R., and Boulet, M., *J. Dairy Sci.*, 1959, **42**, 1390.
13. Rowland, S. J., *J. Dairy Res.*, 1938, **9**, 30.
14. Indian Standard Methods of Test for Dairy Industry, Part II, "Chemical Analysis of Milk," IS : 1479 (Part II) : 1961, pp. 29 and 30.
15. West, T. S., and Sykes, A. S., "Analytical Applications of Diamino-Ethane-Tetra-Acetic Acid," Second Edition, The British Drug Houses Ltd., Poole, Dorset, 1960, p. 76.
16. Harlow, G. A., Noble, C. M., and Wyld, G. E. A., *Anal. Chem.*, 1956, **28**, 784.
17. Kenny, A. D., and Toverud, S. U., *Ibid.*, 1954, **26**, 1059.
18. Collier, R. E., *Chem. & Ind.*, 1955, 587.
19. Ntailianas, H. A., and Whitney, R. McL., abstract of paper presented at the 58th Annual Meeting of the American Dairy Science Association, Manufacturing Section, in *J. Dairy Sci.*, 1963, **46**, 613.

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SHORT PAPERS

Wedge-layer Chromatographic Clean-up of Dinoseb Extracts

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Dinoseb [2-(1-methyl-n-propyl)-4,6-dinitrophenol] is finding increasing use in agriculture as a pre-emergence herbicide, a potato-haulm killer, a pre-harvest desiccant for legumes grown for seed and as a post-emergence selective herbicide on some varieties of peas, beans and certain other crops. Because of a possible use as a desiccant on onions, methods for determining residues in this crop have been investigated. Potter[1] has developed a colorimetric method for determining traces of dinoseb in potatoes; in attempts to extend this method to onions, rather low recoveries were obtained. Although about 80 per cent. of the added dinoseb could be recovered from the separated outer skins of the onions, similar extracts of the onion bulk yielded recoveries of only about 50 per cent. Onions that had been physically denatured by storage at −20° C, with consequent cell-wall rupture, gave only 10 per cent. recovery of added dinoseb. These poor yields were presumably caused by the higher water content of onions (89 to 92 per cent.)[2] as compared to potatoes (75 to 80 per cent.),[3] leading to inefficient partition. In order to obtain the recoveries quoted, a larger amount of sodium carbonate than that indicated by Potter was needed to neutralise the co-extracted trichloroacetic acid.

Other solvent-extraction systems were examined in attempts to eliminate these recovery difficulties. A 3 + 2 mixture of ethyl methyl ketone and hexane has been shown[4] to give good recoveries of organo-phosphorus pesticides. Application of this system to the extraction of dinoseb from fresh and denatured onions gave recoveries of up to 70 per cent., although some coloured interfering materials were also extracted. The use of a 1 + 1 mixture of ethyl methyl ketone and diethyl ether, in which dinoseb is readily soluble both as the free acid and as the sodium salt, gave recoveries of about 90 per cent. It was, however, obvious that a clean-up process was necessary.

Thin-layer chromatographic clean-up on alumina - silica gel plates was carried out with some success. The use of wedge-layer chromatography[5] offered advantages and has been successfully applied to these extracts. In use the concentrated extract is applied as a streak along the thickest edge of a layered plate, the material of which tapers from 2 mm to 100 μ. The high adsorptive capacity of the thicker layer holds back the vegetable extractives while having little or no effect on the migration of the pesticide. Once the dinoseb is free from the interfering materials, development proceeds normally at the usual thin-layer speed.

Wedge-layer plates composed of alumina G, silica gel G, kieselguhr G and mixtures of any two of these three materials have been prepared and examined. Mixtures of silica gel and kieselguhr and of alumina and silica gel were prone to cracking across the wedge, though without marked effect on their chromatographic properties. Alumina and kieselguhr appeared to be of similar physical structure and mixtures of these materials did not show this cracking; they also possessed the necessary adsorptive properties.

Highly activated wedge-layer plates composed of a 1 + 1 mixture of alumina G and kieselguhr G were developed with the mobile solvent previously[6] found suitable for the thin-layer separation of herbicides. The dinoseb travelled close to the solvent front and was clearly separated from its associated interfering materials, the maximum R_F of which was about 0·25. When the developed plate was dried at 120° C the dinoseb appeared in the yellow anionic state as the acetic acid evaporated. The self-indicating dinoseb was then eluted from the absorbent and determined spectrophotometrically.[1] Infrared spectroscopy has been used to confirm the identity and purity of the eluted material.

Method

Apparatus—

Wedge-layer spreading apparatus—The Desaga thin-layer spreading apparatus, available from Camlab Ltd., Cambridge, and modified as described by Abbott and Thomson[5] (see Fig. 1), has been found suitable for preparing wedge-layer plates graded from 2 mm to 100 μ.

Plate-drying oven—An air oven set at 120° C is suitable for activating and drying the wedge-layer plates.

Carrier plates—Glass thin-layer carrier plates, 20 × 20 cm, available from Camlab Ltd., Cambridge.

Top-drive macerator.

Calibrated syringe—Capacity, 1 ml.

Chromatographic tank—As described by Evans.[7]

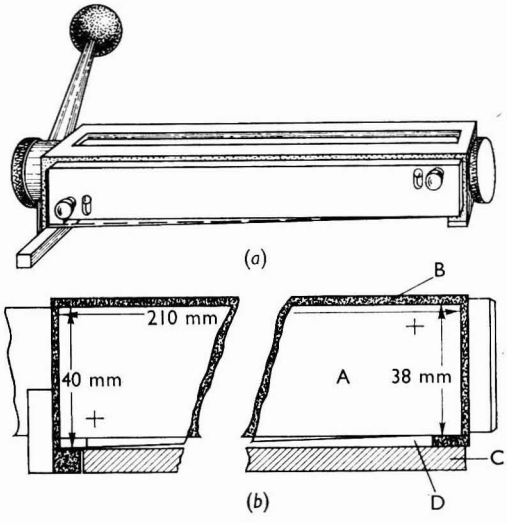

Fig. 1. Diagram of apparatus for preparing wedge-layer plates.

(*a*) Perspex plate attached to Desaga spreader.

(*b*) Plan view of the apparatus: A, Perspex plate; B, spreader; C, glass carrier plate; D, wedge layer

REAGENTS—

Analytical-reagent grade materials should be used whenever possible.

Ethyl methyl ketone.

Diethyl ether.

Alumina G—For thin-layer chromatography, available from E. Merck, Darmstadt.

Kieselguhr G—For thin-layer chromatography, available from E. Merck, Darmstadt.

Mobile solvent—Add 10 ml of liquid paraffin, 30 ml of benzene and 20 ml of glacial acetic acid to 200 ml of cyclohexane.

Sodium sulphate, anhydrous.

Standard dinoseb solution—Prepare a solution containing 20 μg of dinoseb per ml in ethyl methyl ketone.

PROCEDURE—

Preparation of wedge-layer plate—Place 30 g of a 1 + 1 mixture of alumina G and kieselguhr G in a stoppered bottle. Add 60 ml of water and shake the bottle for 2½ minutes. Pour the fluid mix into the spreader and apply a layer to the carrier plate in the usual way. Dry the plate in an oven at 40° C for 20 minutes. Activate the plate at 120° C for 2 hours and allow it to cool in a desiccator over silica gel.

Extraction of dinoseb—Macerate 50 to 100 g of vegetable material with 4 successive 50-ml portions of a 1 + 1 mixture of ethyl methyl ketone and ether. Combine the extracts, dry them with anhydrous sodium sulphate and concentrate them to about 0·5 ml in a Kuderna - Danish evaporator.

Development of wedge-layer plate—By using a 1-ml calibrated syringe, carefully apply the concentrated extract to the plate as a linear streak parallel to that edge of the plate at which the layer is thickest and about 15 mm from it. Re-activate the plate at 120° C for 1 hour and then develop it for 1 hour by ascending-solvent chromatography with the mobile solvent, which has been

allowed to equilibrate in the chromatographic tank. Dry the plate at 120° C for 20 minutes, scrape the yellow dinoseb band from the plate into a small folded filter-paper, and elute it with ethyl methyl ketone. Adjust the volume of the eluate to 10 ml.

Spectrophotometric determination—Determine the optical density of the ethyl methyl ketone solution, obtained as described above, in 1-cm cells at 379 mμ. Use the solvent as a blank solution. Calculate the dinoseb content of the sample by reference to a calibration curve obtained by plotting the optical densities of appropriate amounts of the standard dinoseb solution over the range 0 to 100 μg.

Results

The extraction and clean-up procedure detailed above has been used to determine traces of dinoseb added to several types of sample before they were macerated. The recovery results are given in Table I and are the results of single experiments.

Table I

Recoveries of dinoseb added to various samples

Sample	Weight, g	Dinoseb added, p.p.m.	Dinoseb recovered, p.p.m.	Recovery, per cent.
Onion	75	0·27	0·23	85
Potato	60	0·33	0·26	79
Cucumber	40	0·50	0·40	80
Apple	50	0·40	0·31	78
Water	120	0·17	0·15	88
Soil	100	0·20	0·16	80

Permission to publish this paper has been given by the Government Chemist, Department of Scientific and Industrial Research.

References

1. Potter, J. A., *Analyst*, 1963, **88**, 651.
2. Sherratt, J. G., *Ibid.*, 1943, **68**, 200.
3. Cox, H. E., "The Chemical Analysis of Foods," Fourth Edition, J. & A. Churchill Ltd., London, 1950, p. 117.
4. Egan, H., Hammond, E. W., and Thomson, J., *Analyst*, 1964, **89**, 175.
5. Abbott, D. C., and Thomson, J., *Chem. & Ind.*, 1964, 481.
6. Abbott, D. C., Egan, H., Hammond, E. W., and Thomson, J., *Analyst*, 1964, **89**, 480.
7. Evans, W. H., *Ibid.*, 1962, **87**, 569.

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The Detection of Organo-phosphorus Pesticides on Thin-layer Chromatograms

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Despite the increasing use of thin-layer chromatography for separating, identifying and determining residues of organo-phosphorus pesticides in plant and animal tissues, little has been reported on the specificity and sensitivity of reagents used to detect these compounds. Bäumler and Rippstein[1] used palladium^{II} chloride in dilute hydrochloric acid to detect thiophosphate pesticides, but this reagent, which is not very sensitive, appears to react with many sulphur-containing compounds. Walker and Beroza[2] examined the thin-layer chromatography of sixty-two pesticides, including twenty-seven containing phosphorus, but detected them all by means of three non-specific spray reagents, namely, iodine vapour, bromine vapour - fluorescein, and silver nitrate. With the latter two reagents the sensitivity was generally no better than 1 μg.

Several reagents for locating organo-phosphorus pesticides on paper have been reported, but until recently none of these have been adapted to thin-layer chromatography. Braithwaite[3] has used 2,6-dichloro-*p*-benzoquinone-4-chlorimine, a reagent previously used on paper by Menn, Erwin and Gordon[4] for locating as little as 0·1 μg of certain thiophosphate pesticides on silica-gel layers prepared at pH 4.

Several other reagents have now been investigated for their suitability for use on thin-layer plates, and are reported in this paper. The Hanes - Isherwood reagent,[5] which should be specific for phosphorus-containing esters, was of little use for organo-phosphorus pesticides, since they are not readily hydrolysed. It has not been possible so far to find a method of hydrolysis for use on thin-layer plates, although several modifications were tried, including that of Otter[6] in which *N*-bromosuccinimide is used. The ferric chloride - sulphosalicylic acid reagent of MacRea and McKinley[7] did not have sufficient sensitivity at low levels on silica gel. However, the method originally reported by Wood[8] for detecting compounds forming insoluble complexes with silver nitrate, and that by Cook[9] based on cholinesterase inhibition on paper, have been successfully adapted and extended for use on silica-gel thin-layer plates.

Wood's method is specific for sulphur-containing organo-phosphorus pesticides, although certain naturally occurring sulphur compounds may also react. The sensitivity is 0·2 to 0·1 μg. Oxidation with bromine vapour before application of the silver nitrate was found to yield another, though less sensitive, means of detection. The method described by Cook is specific for cholinesterase inhibitors, and for some compounds investigated, such as diazinon, it was extremely sensitive. Further, since the spots are transferred to a clean sheet of paper, this method is less susceptible to interference by extraneous material not completely removed by the clean-up procedure used. In general, these two methods were developed for use with plates of silica gel without binder. Any adaptations for use with alumina are indicated, but the reagents appear to be less sensitive on this medium. No satisfactory reagent could be found for detecting schradan.

Experimental

The organo-phosphorus pesticides investigated are listed in Table I by their recognised common names,[10] with the exception of *O,O*-dimethyl *S*-2-(1-methylcarbamoylethylthio)-ethyl phosphorothiolate, for which the proprietary name Vamidothion is used. The technical products were used, and were prepared for spotting as 0·1 per cent. w/v solutions in analytical-reagent grade ethyl acetate; these solutions were diluted when necessary with n-hexane.

Table I

Comparison of R_F values for different conditions and limits of detection

Pesticide	R_F values for development with benzene - acetone (9 + 1) mixture— on silica gel H*	R_F values for development with benzene - acetone (9 + 1) mixture— on alumina†	Limits of detection, μg, on silica gel H by using— method A§	Limits of detection, μg, on silica gel H by using— method B	Limits of detection, μg, on silica gel H by using— method C
Azinphos-methyl	0·40	0·53	0·1 (blue)	1	0·5
Demeton-O	0·60	0·73	0·2 (mauve)	1	0·2
Demeton-S	0·19	0·36	0·2 (blue)	1	0·5
Diazinon	0·38	0·71	0·2 (mauve)	0·2	<0·1
Dimethoate	0·03	0·10	<0·1 (blue)	0·2	0·2
Ethion	0·62	0·76	0·1 (mauve)	1	0·5
Fenchlorphos	0·56	0·73	0·2 (mauve)	1	<0·1
Malathion	0·45	0·64	0·1 (mauve)	1	0·5
Mevinphos	0·10	—	—	1	0·2
Morphothion	0·07	0·15	<0·1 (blue)	0·2	1
Parathion-methyl	0·43	0·68	0·1 (mauve)	1	0·5
Phenkapton	0·56	0·75	0·1 (blue)	1	0·2
Phorate	0·69	0·73	0·2 (blue)	1	1
Phosphamidon	0·10	—	0·2 (blue)	—	1
Schradan	—	—	—	—	—
Vamidothion‡	0	0	0·1 (blue)	0·2	—
Vamidothion sulphone	0	0	0·1 (blue)	0·2	—

* R_F of Sudan red = 0·53.
† R_F of Sudan red = 0·70.
‡ *O,O*-dimethyl *S*-2-(1-methylcarbamoylethylthio)-ethyl phosphorothiolate.
§ Colour of spot in parentheses.

Procedure—

Glass plates, 20-cm square, were spread with silica gel H (Merck and Co. Ltd.) or neutral alumina without binder (M. Woelm) 250 μ thick, and after air-drying, they were activated at 125° C for 30 minutes before use. The pesticides were spotted in various amounts in a row 2 cm

from the bottom of each plate together with a mixture of Sudan red, indophenol blue and *p*-dimethylaminoazobenzene as a reference standard. A range of volatile solvent mixtures, *e.g.*, 10 per cent. v/v acetone in chloroform, benzene or n-hexane, were used to develop the plates to a distance of 10 cm in a closed tank with absorbent paper liners. After the plate had been dried, oxidation was, if required, carried out with bromine vapour from a 5 per cent. v/v solution of bromine in carbon tetrachloride. Final traces of bromine were always removed by a cold air draught before any other reactions were carried out. The R_F value for each compound in each solvent was noted in relation to the R_F value of Sudan red, thus compensating[11] for variations of plate thickness, temperature, etc. The R_F values found were, in general, similar to those of Walker and Beroza,[1] and are therefore not quoted in full. For illustration, the R_F values for development with 10 per cent. acetone in benzene on silica gel and alumina are listed in Table I. The Table also lists the minimum amount of pesticide detectable by each of the three chromogenic reagents.

Detection of organo-phosphorus pesticides

Reagents—

Bromophenol blue reagent—A portion (0·05 g) of bromophenol blue was dissolved in 10 ml of acetone. The solution was then diluted to 100 ml with a 1 per cent. w/v solution of silver nitrate in 3 + 1 v/v aqueous acetone.

Dip-mixture reagent—This consisted of a mixture of 20 ml of outdated pooled human blood plasma, which had been stored in a refrigerator, 60 ml of water and 5 ml of a 0·5 per cent. w/v solution of bromothymol blue in 0·1 N sodium hydroxide. This solution was freshly made up before each experiment.

Acetylcholine bromide spray reagent—A 2 per cent. w/v aqueous solution of acetylcholine was used. This reagent is stable for several weeks if stored in a refrigerator.

Method A—

Silica-gel plates were sprayed with bromophenol blue reagent until they were an even blue colour. After they had been dried at 80° C for 10 minutes, the background colour was removed by spraying them with 5 per cent. aqueous acetic acid to reveal blue or mauve spots for all the sulphur-containing organo-phosphorus pesticides indicated in Table I. At low concentrations, approximately 0·5 μg, the colour of the spots was heightened by finally exposing the plate for several minutes to ultraviolet radiation (Hanovia Chromatolite, with filters removed), when the background turns brown. When alumina plates were sprayed with bromophenol blue reagent, coloured spots were discernible on a blue background. However, acetic acid was not suitable for decolorising the background and this was effected by bringing the alumina *briefly* into contact with bromine vapour. The reagent was slightly less sensitive on alumina than on silica gel, but most pesticides were still detectable at the 0·5 μg level.

Method B—

When silica-gel plates were exposed to bromine vapour for 30 seconds before being sprayed with bromophenol blue reagent, the majority of the pesticides examined showed as yellow spots on a blue background, provided the amount of pesticide present was 1 μg or more. Omission of silver nitrate from the reagent did not alter this in any way. The bromophenol blue could be replaced by similar indicators, *e.g.*, bromocresol green, for use as described above. This reagent was not suitable for use on alumina plates. The formation of the yellow spots is probably caused by the sulphenyl bromides, formed on the plate under anhydrous conditions by the interaction of bromine and phosphorothioates,[12] being subsequently hydrolysed by aqueous acetone to yield hydrobromic acid.

Method C—

Sheets of Whatman 3MM chromatographic paper, 29 × 20 cm, were lightly marked in pencil to show the origin, positions of spotting and the line of the solvent front on the plate to be treated. The sheets were then dipped in the dip-mixture reagent. Any excess of reagent was removed by gently wiping the paper with a sheet of filter-paper. After the silica-gel plate had been exposed to bromine vapour for 30 seconds, and then lightly sprayed with water, the marked filter-paper was placed over the layer, and covered by a clean glass plate. Even pressure was applied for 30 minutes by means of a weight of 2 to 3 kg, and then the paper was peeled from the silica-gel plate and lightly sprayed with the acetylcholine bromide spray reagent. When this paper was

hung in a moist atmosphere blue spots slowly appeared on a yellow background where cholinesterase inhibition had occurred. These spots were most prominent after about 30 minutes, and then gradually faded. When bromine-vapour oxidation was omitted only diazinon, mevinphos and phosphamidon gave spots at the lowest levels indicated in Table I. Transfers of inhibition in this manner from alumina plates appeared to be more difficult, and only azinphos-methyl, diazinon, ethion, fenchlorphos, phenkapton and phorate gave responses at the 2-μg level. All attempts to cause inhibition of this type directly on the plates, including the use of several other indicators, were unsuccessful.

British Cyanamide Ltd., Dow Agrochemicals Ltd., Fisons Pest Control Ltd., May and Baker Ltd., The Murphy Chemical Co. Ltd. and The Shell Chemical Co. Ltd. are thanked for gifts of technical-grade pesticides.

References

1. Bäumler, J., and Rippstein, S., *Helv. Chim. Acta*, 1961, **44**, 1162.
2. Walker, K. C., and Beroza, M., *J. Ass. Off. Agric. Chem.*, 1963, **46**, 250.
3. Braithwaite, D. P., *Nature*, 1963, **200**, 1011.
4. Menn, J. J., Erwin, W. R., and Gordon, H. T., *J. Agric. Food Chem.*, 1957, **5**, 601.
5. Hanes, C. S., and Isherwood, F. A., *Nature*, 1949, **164**, 1107.
6. Otter, I. K. H., *Ibid.*, 1955, **176**, 1078.
7. MacRae, H. F., and McKinley, W. P., *J. Ass. Off. Agric. Chem.*, 1961, **44**, 207.
8. Wood, T., *Nature*, 1955, **176**, 175.
9. Cook, J. W., *J. Ass. Off. Agric. Chem.*, 1955, **38**, 150.
10. "Recommended Common Names for Pesticides," British Standard 1831 : 1961.
11. Stahl, E., *ChemikerZtg.*, 1958, **82**, 323; *Chem. Abstr.*, 1959, **53**, 27*c*.
12. Stirling, C. J. M., *J. Chem. Soc.*, 1957, 3597.

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Use of a Cation-exchange Resin in the Determination of Urinary Ascorbic Acid

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The determination of urinary ascorbic acid (vitamin C) has always presented certain difficulties. The most widely used method is that based on the reduction of an acidic solution of the redox dye 2,6-dichlorophenolindophenol by the ascorbic acid.[1,2,3] Urine contains interfering substances that introduce substantial errors when the vitamin is measured by this method.

This paper describes a preliminary treatment of the urine with a cation-exchange resin before the ascorbic acid content is measured with indophenol dye. This removes the whole of the yellow urinary pigment together with about 30 per cent. of the original capacity of the urine to reduce the dye. Since, under the same conditions, there is no loss of added ascorbic acid during the resin treatment, it is assumed that the change in the capacity of the urine to reduce the indophenol dye is due to removal of interfering substances.

Method

Apparatus—

Resin column—The ion-exchange resin is contained in a glass chromatography tube of length 30 cm and internal diameter 1 cm.

Photo-electric colorimeter—An Evans Electroselenium Ltd. Spectra or any similar instrument fitted with cells of capacity 8·5 ml and optical path 20 mm is used.

Reagents—

Cation-exchange resin—Zeo-Karb 225 (Permutit, London) of mesh size 52 to 100.

2,6-*Dichlorophenolindophenol dye*—Prepare a stock solution (approximate strength, 1 ml $\equiv$ 0·2 mg of ascorbic acid) by dissolving 200 mg of 2,6-dichlorophenolindophenol in 500 ml of water. Standardise the solution by titration against standard ascorbic acid in 2 per cent.

metaphosphoric acid solution. Store it at 2° C in the dark. Prepare working solutions (1 ml ≡ 0·02 mg of ascorbic acid) from the stock solution as required by dilution with water.

Ascorbic acid oxidase—Make a fresh preparation as described by Booth and Constable.[4] A 2-ml portion of the extract added to 20 ml of urine destroys all the ascorbic acid in 15 minutes.

Metaphosphoric acid—Prepare 20 per cent. and 10 per cent. w/v solutions in water.

Phosphate buffer, pH 2·3—Dissolve 188 g of citric acid and 30·8 g of anhydrous disodium hydrogen orthophosphate in 500 ml of water. Filter the solution before use.

Sodium hydroxide, 2 N.

Hydrochloric acid, 2 N.

PROCEDURE—

Place a plug of glass wool at the bottom of the chromatography tube and directly over it a 1-cm layer of acid-washed sand. Cover the surface of the sand with a disc of filter-paper. Prepare a slurry of the resin in water and pour it carefully into the tube. As the resin settles out, gently pack it into position with a glass rod; repeat this procedure until the height of the resin column in the tube is 10 cm.

Activate the column by washing it, first with 30 ml of 2 N sodium hydroxide and then with water until the washings are no longer alkaline. Then wash it with 30 ml of 2 N hydrochloric acid and finally water, until the washings are neutral. The column is then ready for use.

By means of a pipette, place 5 to 7 ml of urine that contains 2 per cent. of metaphosphoric acid on to the column and collect the effluent in 2 ml of 20 per cent. metaphosphoric acid in a graduated vessel. Wash the column with water until the effluent is no longer acid. The total volume of the treated urine plus washings should not exceed 15 to 20 ml; measure this final volume accurately. Determine the ascorbic acid content of a portion of this solution. For solutions containing more than 0·02 mg of ascorbic acid per ml the visual titration method[1] may be used. However, for normal urines the photometric method is more satisfactory. The procedure used is a modification of the one used by Bessey.[2,5]

Make the determination at 520 mμ. Set the instrument to zero with 3 ml of 2 per cent. metaphosphoric acid, 2 ml of water and 2 ml of buffer in the blank cell. Place a second cell that contains 2 ml of buffer and 3 ml of the urine solution in position in the instrument and quickly add 2 ml of dye (1 ml ≡ 0·02 mg of ascorbic acid) from a blow-out pipette. Carefully, but thoroughly, mix the contents of the cell with a small glass rod and take the reading 15 seconds after the moment of mixing. Calculate the amount of ascorbic acid present by reference to a standard curve constructed by treating known amounts of ascorbic acid with the dye under conditions of the determination.

RESULTS

The method has been applied to many normal urines. Recoveries of added ascorbic acid have also been made, as described below.

TABLE I

EFFECT OF COLUMN TREATMENT ON (*i*) CAPACITY OF URINE FOR REDUCING INDOPHENOL DYE AND (*ii*) RECOVERY OF ADDED ASCORBIC ACID

	(*i*)		(*ii*)			
	Ascorbic acid content, mg per 100 ml of urine		Ascorbic acid added, mg per 100 ml of urine	Ascorbic acid, mg per 100 ml of urine		
Sample	Untreated urine (*a*)	After column treatment (*b*)	(*c*)	after column treatment (*d*)	Recovered (*d* - *b*)	Recovery, per cent.
1	0·55	0·28	0·48	0·77	0·49	102
2	0·80	0·56	0·69	1·25	0·69	100
3	0·48	0·23	0·93	1·12	0·89	96
4	1·63	1·25	1·12	2·38	1·13	101
5	1·45	0·94	1·35	2·26	1·32	98
6	1·22	0·84	1·42	2·25	1·41	99
7	1·84	1·33	1·80	3·13	1·80	100
8	0·80	0·32	1·91	2·21	1·89	99
9	—	—	0·88	0·87	0·87	99
10	—	—	2·15	2·11	2·11	98

A portion (20 ml) of urine was treated with 5 ml of 10 per cent. metaphosphoric acid to give a final concentration of 2 per cent. metaphosphoric acid. A 5-ml aliquot of this acidified urine was added to 2 ml of 20 per cent. metaphosphoric acid and the volume made up accurately to 16 ml. The "apparent ascorbic acid content" of this solution was determined by using the photometric method. Results for eight normal urines are given in Table I, column (*a*). A further 5-ml of the acidified urine were allowed to percolate through the column as described above and the effluent made up to 16 ml. Ascorbic acid was determined in a 3-ml portion. The results, given in Table I, column (*b*), show that between 20 and 50 per cent. of the original dye-reducing capacity of the urine had been removed by the resin.

Standard solutions of ascorbic acid (freshly made in 10 per cent. metaphosphoric acid), were used in the recovery tests. Portions (5 ml) of such a solution were added to a second 20 ml of the urine and 5 ml of the resultant solution subjected to the column treatment. The results in column (*d*) thus represent the original urinary ascorbic acid, column (*b*), *plus* added ascorbic acid, column (*c*).

Results 1 to 8 are typical recoveries obtained within the usual range of ascorbic acid in urine. All results are expressed as mg of ascorbic acid per 100 ml of urine. Results 9 and 10 were obtained by using ascorbic acid in 2 per cent. metaphosphoric acid but without any urine.

TABLE II

COMPARISON OF VALUES FOR ASCORBIC ACID CONTENT OF VARIOUSLY TREATED URINES

	Ascorbic acid content, mg per 100 ml of urine		
Sample	Untreated urine (*a*)	After ascorbic oxidase treatment (*b*)	After resin treatment (*c*)
1	3·00	0·98	1·20
2	2·10	1·15	1·28
3	5·65	4·19	4·30
4*	16·20	13·61	13·21

* Urine sample 4 was from a subject dosed 10 hours previously with 100 mg of ascorbic acid.

Certain urines were also treated with ascorbic acid oxidase to destroy the ascorbic acid, and the true ascorbic acid content was calculated by subtracting the residual indophenol titration from the original one (see Table II).

DISCUSSION

The findings summarised above indicate that the classical indophenol method as generally applied to normal urines gives vitamin C values that are from 25 to 100 per cent. too high. Substances that reduce indophenol dye other than ascorbic acid appear to be present. There is, for example, a residual titre in the urine after treatment with the enzyme ascorbic acid oxidase to destroy ascorbic acid (see Table II, columns *a* and *b*). Treatment of the urine with a cation-exchange resin, as described in this paper, appears to remove the bulk of such interfering substances (see Tables I and II). Recovery tests on added ascorbic acid over the range found in normal urines gave values of 96 to 102 per cent.

A single determination involving the resin treatment should be completed in 12 minutes, and at least five determinations can be done before re-activation of the resin becomes necessary.

REFERENCES

1. Harris, L. J., and Ray, S., *Lancet*, 1935, **228**, 71.
2. Bessey, O. A., *J. Biol. Chem.*, 1938, **126**, 771.
3. Bland, M. N., Constable, B. J., Harris, L. J., and Hughes, R. E., Proceedings of the 12th International Congress on Chemistry (Food and Nutrition Section), New York, 1951, p. 155.
4. Booth, V. H., and Constable, B. J., *Biochem. J.*, 1960, **76**, 206.
5. Hughes, R. E., *Ibid.*, 1956, **64**, 203.

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The Determination of Boron by a Pyrohydrolysis Technique

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Boron can be determined by conventional methods if dissolution of the sample is possible; in some instances, however, this is extremely difficult, involving fusions that may result in high or variable blank values.

Similar problems have arisen in the determination of halides in inorganic materials, and several workers[1,2,3,4] have successively used a pyrohydrolysis method to isolate the halide from the bulk of the sample. Boron in glass has been determined as boric oxide by a pyrohydrolysis technique,[5] and the idea of recovering boron by pyrohydrolysis of the materials in which I was interested appeared to offer a solution to the problem, and this was investigated.

This paper briefly describes the successful outcome of this work, but it must be pointed out that after this independent approach had been made, other workers[6] had, almost concurrently, successfully developed a similar procedure.

Experimental

When the sample (preferably, though not necessarily, in a finely divided form) is subjected to pyrohydrolysis at 1400° C it liberates its boron as boric acid into the steam, which is then condensed. The distillate can be examined by any of the conventional methods for boron, *e.g.*, by the standard sodium hydroxide - mannitol titration for boron contents greater than 0·5 per cent. w/w and by colorimetric methods for contents less than 0·5 per cent. w/w.[7,8,9]

A 0·125-inch thick Inconel tube, though still steam-tight after 24 hours of operating conditions, scaled considerably, and an 18 - 8 boron-free stainless-steel tube of similar thickness was attacked even more quickly. Platinum, although suitable for the conditions stated, was disregarded owing to anticipated difficulties with platinum - glass connections.

Finally it was found that a 0·065-inch thick quartz tube remained steam-tight even when the temperature was raised from 1050° to 1400° C. By ensuring that the temperature of the tube after installation always remained above 1000° C, a working life of at least 2000 hours was obtained. The temperatures were recorded by an optical pyrometer, focused on the platinum boat through a viewing tunnel in the centre of the furnace during the actual pyrohydrolysis of the sample.

With pyrohydrolysis at 1050° C, the time to recover the boron was about 210 minutes when the distillate was collected at a rate of 1 to 3 ml per minute. Increasing the collecting rate to 3 to 6 ml per minute did not appreciably alter the recovery rate of boron, whereas by increasing the pyrohydrolysis temperature to 1400° C and by using a collecting rate of 2 ml per minute, recovery time for boron was reduced to about 90 minutes (see Table I).

Table I

Effect of time on recovery of boron by pyrohydrolysis

Cumulative time of pyrohydrolysis, minutes	Percentage of boron by weight recovered from—		
	Boron carbide	Zirconium diboride	Zirconium diboride cermet, 2 per cent. w/w
30	41·01	11·57	0·89
60	72·54	15·64	1·73
80	77·74	18·40	1·93
90	77·74	18·40	1·93
120	77·74	18·40	1·93

Williams, Campbell and Magliocca[5] used U_3O_8 as an accelerator together with other additives to obtain boron recovery by this method at 1050° C. At 1400° C the boron recovery is completed in about 90 minutes, so these additives have been omitted, thereby reducing any contamination from U_3O_8 and additives that may give rise to variable blank values.

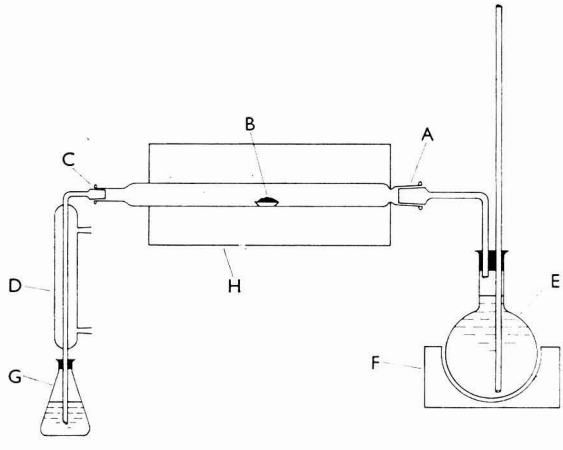
When boron was determined by titration after pyrohydrolysis, the typical blank value was 0·55 ml of 0·1 N sodium hydroxide. This blank value was not, however, attributable to boron, since with a colorimetric finish[7] the blank value was less than 5 μg of boron.

Method

Apparatus—

The specimen boats were prepared from platinum foil about 0·01-inch thick (approximate dimensions 1·0 × 0·375 × 0·375 inch). The silica furnace tube was 30 inches long, 1 inch in diameter and had a 0·065-inch wall thickness, and was fitted with a B29-necked silica cone at the steam-generator end and a B19-necked silica cone at the condenser end. The B24-necked 500-ml collecting flask was also of silica. The condenser and the 3-litre steam-generating flask were of Pyrex glassware (blank determinations carried out on the apparatus and coloured with 1,1-dianthrimide gave no evidence of boron contamination from the glassware).

The furnace was heated by four Crusilite elements, parallel with, and equidistant from the quartz furnace tube, and controlled by a variable transformer.



A = B29-necked silica tube, 30 inches long, 1 inch in diameter
B = Specimen boat
C = B19 joint
D = Condenser
E = Steam generator, B34-necked 3-litre flask
F = Heating jacket
G = 250-ml silica B24-necked conical flask
H = Furnace operated at 1400°C

Fig. 1. Apparatus for the pyrohydrolysis of boron

Procedure—

Assemble the apparatus as shown in Fig. 1 except for the steam generator, which should be filled with water and boiled for about 15 minutes to ensure complete purging of carbon dioxide.

Introduce the platinum-foil boat into the hot zone of the furnace tube and connect the steam generator to the apparatus. Collect the distillate at a rate of 2 ml per minute into 10 ml of 0·1 N sodium hydroxide and 10 ml of de-mineralised water contained in the B24-necked 500-ml flask, while the furnace temperature is maintained at 1400° C for 90 minutes. Stopper the flask after the separation and retain the solution in the flask for the blank determination.

Purge the system with nitrogen to remove any pockets of hydrogen.

Remove the platinum boat, allow it to cool and weigh the sample into it (the amount selected should depend upon the anticipated boron content; see Table II). Re-connect the steam generator and collect the distillate as before.

After pyrohydrolysis, analyse the distillates by using either the titration or the colorimetric determination, depending upon the anticipated boron content (see Table II).

TABLE II

SAMPLES INVESTIGATED, WEIGHTS TAKEN, FORM OF SAMPLES AND RESULTS OBTAINED

Sample	Form	Weight of sample, g	Boron, per cent. w/w, obtained by pyrohydrolysis with finish—		Boron, per cent. w/w, obtained by—	
			titrimetric	colorimetric	fusion	acid attack
Boron-10	Powder	0·1	92·7, 93·4	—	93·0, 92·4	—
Boron-10	Powder	0·1	95·3, 96·0	—	96·1, 95·8	—
1·2 per cent. w/w boron steel	0·0010-inch sheet	1 to 2	1·30, 1·29	—	1·30	—
Zirconium diboride ..	Powder	0·1	18·40, 18·40, 18·14	—	17·9	—
Boron carbide	Powder	0·1	77·90, 78·00	—	77·93	—
0·5 per cent. w/w of boron in zirconium	Millings	1·0	0·556	0·555	—	0·540
2·5 per cent. w/w of boron in boron carbide cermet	Pin	1 to 2	2·74, 2·81	—	2·71, 2·81	—
2·5 per cent. w/w of boron in zirconium diboride cermet	Pin	1 to 2	2·58, 2·49	—	2·61, 2·57	—
4·0 per cent. w/w of boron in boron carbide cermet	Pin	1 to 2	3·78, 3·68	—	3·71, 3·75	—
Murex welding electrode, nominal boron content, 0·0036 per cent. ..	Turnings	5	—	0·0040	—	—
Welding rods, K.S.10 ..	Turnings	5	—	0·0008	—	—
Alumina insulation rods ..	Powder	5	—	0·0019, 0·0021	—	—

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REFERENCES

1. Warf, J. C., Cline, W. D., and Tevebaugh, R. D., *Anal. Chem.*, 1954, **26**, 342.
2. Susano, C. D., White, J. C., and Lee, J. E., jun., *Ibid.*, 1955, **27**, 453.
3. Powell, R. H., and Menis, O., *Ibid.*, 1958, **30**, 1546.
4. Bennett, H., and Hawley, W. G., *Trans. Brit. Ceram. Soc.*, 1963, **62**, 397.
5. Williams, J. P., Campbell, E. E., and Magliocca, T. S., *Anal. Chem.*, 1959, **31**, 1560.
6. Wieder Kehr, V. R., and Goward, G. W., paper presented at the Fourth Conference on Analytical Chemistry in Nuclear Technology, Pittsburg, Pa., October, 1960.
7. Hayes, M. R., and Metcalfe, J., *Analyst*, 1963, **88**, 471.
8. Elwell, W. T., and Wood, D. F., *Ibid.*, 1963, **88**, 475.
9. Snell, F. D., and Snell, C. T., "Colorimetric Methods of Analysis: Including Photometric Methods," D. Van Nostrand Co. Ltd., Princeton, N.J., New York, Toronto and London, 1959, Volume IIA, pp. 594 and 597.

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Book Reviews

INTERNATIONAL ENCYCLOPAEDIA OF CHEMICAL SCIENCE. Pp. viii + 1331. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Company Inc. 1964. Price £11 15s.

"True, I know much, yet would I all things know." So Goethe has Wagner say to Faust; a sentiment that has appealed to many minds and possibly stimulated encyclopaedists to produce their voluminous treatises *de omnibus rebus, et quibusdam aliis*. Etymologically, an encyclopaedia should contain the whole circle of knowledge, a state of affairs that might have been realisable in Plato's time, but has long ceased to have any possibility of being realised, so that encyclopaedias have become sectional. Even so, and with the galaxy of brains that goes into their compilation, they cannot achieve completion. And if they show us how much we do not know, they also show us how much there is to know and what little hope we have as individuals of knowing it all; so that the most we can look for is some practical help in bridging some of the gaps even if the circle of knowledge can never be completed. For the scientist, in particular, new knowledge frequently involves new terminology (some would say jargon), esoteric, but nevertheless of interest to the enquiring mind. These are the people whom the present volume aims to serve, and the extent to which it will succeed depends on what one expects. It is described as "integrating recent developments in theory with practical reference information"; this it does very well, with a concentration on fundamental conceptions and an emphasis on physical and theoretical chemistry (with its mathematics). As to the *quibusdam aliis*, "the principles of structure and mechanism, chemical elements, their inorganic and organic compounds, reactions, processes, tests are all thoroughly covered."

This appears too much to expect in a mere 1300 pages, so I took a pile of recent publications and journals and looked up the terms with which I was unfamiliar, or only vaguely familiar. I was agreeably surprised to find how many terms were covered, but there were some surprising omissions, for instance, autocoherent molecular orbitals, Hakala's rule, Kassel theory (free-radicals), Mössbauer effect, nitrogen mustard, radiomimetic compounds and, in general, names of organic compounds of natural origin, *e.g.*, interferon, humulins and individual antibiotics. The increasing use of initials in science no less than in world politics would have made their listing worthwhile, and we could surely do without such definitions as abrasion, air-bath, hot-plate, roast, odour and acetate; perhaps it was a sense of humour that included "bottle," with which most of us have been familiar since infancy. Organic chemistry was in fact represented for the most part by radical names and name reactions, all of which is very useful information, but is hardly thorough coverage. On the other hand, there is some useful information on organic compounds of boron and phosphorus, but surprisingly none on those of tin. This, however, is straining at a gnat in view of the great mass of information supplied. It makes one feel with Charles Lamb, that "in everything that relates to science, I am a whole encyclopaedia behind the rest of the world." This volume appears too late for him, but not for many of us.

An original and valuable feature is a series of vocabularies of scientific and technical terms in French, German, Spanish and Russian (why not Italian?), giving the English equivalents under which they may be found in this volume.

Altogether a good book to have at hand by the chemist in the laboratory or the library. Misprints are few but there is some inconsistency in the insertion of the double bonds in aromatic rings that might puzzle a neophyte.

J. I. M. JONES

ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM. By ROSS W. MOSHIER. Pp. iv + 278. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1964. Price 90s.

The two metals in question are always found together in nature, and it is not surprising that the close similarity of the reactions of their compounds has *tantalised* chemists for over a century.

The analytical chemistry of these "earth-acid" elements made little advance, if any, since the classical separation of Marignac in 1866, until publication of the results of a seventeen-year study by Schoeller and his associates, half a century later. The discovery of the radioactive isotopes niobium-95 and tantalum-182 during the early 1940s, and their use as tracers in separation studies, provided the analyst with an invaluable tool in this particular field.

In 1949, Kraus and Moore announced the successful separation of niobium from tantalum

by using an ion-exchange method, and at about the same time details of the selective solvent-extraction and spectrophotometric properties of these two metals began to appear in the technical literature. More recently several good reviews have been published.

Any book dealing with the analytical chemistry of niobium and tantalum would be criticised if it approached the subject without this historical survey, and this book fulfils that requirement in the detail it merits.

The subjects covered in the 19 chapters range from properties of the two metals and their compounds, with special reference to compounds of analytical interest, polarographic, colorimetric (new reagents) and titrimetric methods to spectrographic procedures. For good measure a chapter is devoted to the determination of impurities associated with niobium - tantalum-bearing products of commercial interest.

A list of selected references, amounting to over 550, is appended to each chapter, and this is supplemented by a collected list of authors named alphabetically at the end of the book.

Chapter titles and sub-headings of the book are well chosen, and credit is due to the author and general editors for adding yet another useful monograph to the series. W. T. ELWELL

THE INORGANIC CHEMISTRY OF NITROGEN. By WILLIAM L. JOLLY. Pp. xii + 124. New York and Amsterdam: W. A. Benjamin Inc. 1964. Price $5.75.

This is a volume in the series on physical inorganic chemistry that aims to give the more theoretical background to inorganic chemistry. After the first volume, which was entirely theoretical, there are to be several volumes devoted to special aspects of the subject, and this is one such volume on nitrogen.

At first sight the book seems to be very superficial in its treatment of the chemistry of nitrogen, and I was somewhat disappointed to find some sections dismissed rather summarily. The book is clearly not for the expert in the field, but rather for the person who wishes to know the trends of the subject. It is well written, sound as far as it goes, and each chapter has several useful references for further reading.

The best features of the book are to be found in the first 6 chapters on the unique features of nitrogen, elementary nitrogen, ammonia, nitrogen oxides and oxy-acids, etc., but those on sulphur - nitrogen, phosphorus - nitrogen, carbon - nitrogen and boron - nitrogen compounds are most disappointing, especially in view of recent developments. F. H. POLLARD

TRINKBRANNTWEINE UND LIKÖRE. By H. WÜSTENFELD and Prof. Dr. GEORG HAESELER. Fourth Edition. Pp. xx + 623. Berlin and Hamburg: Verlag Paul Parey. 1964. Price (paper) DM 74; (cloth) DM 78.

This volume may, for all practical purposes be divided into sections dealing with the preparation of spirits and liqueurs, their analytical composition, laboratory control, analysis of raw materials and regulations pertaining to their composition.

The preparation is treated firstly from a historical standpoint and is accompanied by numerous drawings of the apparatus once used. There follow chapters dealing with the theoretical considerations of distillation and the composition of a large number of products. These include the more common ones such as whisky, rum and vodka together with the more exotic types such as kirschwasser and juniper wine. A typical flow chart of distillation processes in current use is to be found at the beginning of this chapter.

The distillation of alcoholic liquors is the subject of the next chapter, which is followed by a comprehensive survey of the preparation and analytical properties of the essential oils encountered in such products. This chapter also includes some useful tables of the composition of various worts and liquors obtained by the more modern techniques such as gas chromatography.

The section dealing with laboratory control is of great value to the analyst, and detailed methods for the determination of a large number of constituents, including necessary modifications to allow for the type of product under examination, are to be found. The determination of the alcohol content of various liquors is explained in great detail and is illustrated by numerous worked examples.

The analysis of the raw materials from the water used in the preparation to the preservatives and colours in the final product conclude this volume together with a list of definitions and abstracts from regulations in force concerning their composition.

Although this is not a book that will be purchased for its "readability," unless the purchaser, unlike myself, is fluent in technical German, it is a useful reference book on this intriguing subject.

J. H. SHELTON

CHROMATOGRAPHIC STEROL ANALYSIS AS APPLIED TO THE INVESTIGATION OF MILK FAT AND OTHER OILS AND FATS. By J. W. COPIUS PEEREBOOM. Pp. xii + 157. The Netherlands: Centrum Voor Landbouwpublikaties en Landbouwdocumentatie. 1963. Price D.fl. 11·25.

This book particularly deals with chromatographic separation of sterols and methods of identifying them in the general subject of analysis of fats.

The first section outlines classical analytical methods for sterols, including gravimetric digitonide separation and colorimetric methods based on the Liebermann - Burchardt reaction.

The second part deals with chromatographic separation based on absorption chromatography and paper chromatography, and special reference is given to the various solvent systems that have been found of value in this field.

Elaboration of R_M and R_F values is discussed, and the identification of unknown sterols from such knowledge is listed.

The application of chromatographic sterol separation to the analysis of fat mixtures is liberally treated. This section is of special value to those interested in the detection of animal and vegetable fats.

Thin-layer chromatography of the sterols has been shown to be of special importance in the differentiation of these closely related substances, and the technique involved is adequately dealt with, *e.g.*, normal and reversed-phase systems, separation as acetates or acetate bromide and semi-quantitative evaluations. The book ends with a chapter on analysis of specialised phytosterol mixtures.

It is well printed and the graphs and tables are quite clear. It is a competent job and is recommended to those engaged in fat analysis. It would be of special value to persons interested in cholesterol-metabolism studies in relation to coronary heart disease and other so-called diseases of civilisation.

R. F. MILTON

MECHANISMS OF OXIDATION OF ORGANIC COMPOUNDS. By W. A. WATERS, M.Sc., Sc.D., F.R.S. Pp. viii + 152. London: Methuen & Co. Ltd.; New York: John Wiley & Sons Inc. 1964. Price 25s.

This volume can be thoroughly recommended as giving an up-to-date account of the various reaction mechanisms operative in the oxidation of the principal types of organic compounds. Although written primarily with the interests of organic chemists in mind, analysts concerned with functional-group analysis of organic compounds could frequently refer to it with advantage. The text is written in a convincing style, and, for me, the exposition was facilitated by the clear printing of the diagrams and equations used to formulate the various reaction mechanisms.

F. G. ANGELL

Errata

JULY (1964) ISSUE, p. 489, 3rd line from foot of page. *For* "18 × 9 inches" *read* "18 × 9 × 9 inches".

IBID., p. 489, last line of page. *For* "chrome - alumel" *read* "chromel - alumel".

IBID., p. 490, 2nd line. *For* "slightly into the furnace" *read* "into the centre of the furnace".

IBID., p. 490, 3rd line. *For* "are" *read* "were".

IBID., p. 492, Table V, heading to 5th column. *For* "open-tube" *read* "sealed-tube".

IBID., p. 494, 7th line. *For* "Dr. I. J. M. Muir" *read* "Dr. I. H. M. Muir".

AUGUST (1964) ISSUE, p. 521, 3rd table of analytical results. *For* "$C_3H_5NO_3$" *read* "$C_3H_7NO_3$".

Notice to Authors

THE Society publishes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Such papers may describe original work or may present in review form a critical evaluation of the existing state of knowledge on a particular facet of analytical chemistry. Papers may be submitted for publication by members of the Society or by non-members.

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Descriptions of new methods should be supported by experimental results showing accuracy, precision and selectivity.

The recommended order of presentation is as indicated below—

(*a*) Synopsis.

(*b*) Statement of object of investigation and, if necessary, historical introduction and account of preliminary experimental work; these need be no longer than is necessary for the understanding of the new material.

(*c*) Description of method. When working details are given, they should, if possible, be given in the imperative mood. Well known procedures must not be described in detail.

(*d*) Presentation of results.

(*e*) Statistical analysis of results. Any statistical evaluation of results should be in accordance with accepted practice.

(*f*) Discussion of scope and validity.

(*g*) Summary and conclusions.

Tables, diagrams, etc.—The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns may often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables must be supplied with titles and be so set out as to be understandable without reference to the text.

* Rules for nomenclature in "Handbook for Chemical Society Authors 1961" (price 21s. from the Chemical Society, Burlington House, London, W.1) are followed. The Shorter Oxford English Dictionary is followed for spelling, but some words are given that Dictionary's secondary alternative spelling.

Tables or graphs may be used, but not both for the same set of results, unless important additional information is given by so doing.

In general, graphs should have a reasonable number of co-ordinate lines, and not only the two main axes. The information given by a stright-line calibration graph can usually be conveyed adequately as an equation in the text.

Diagrams and graphs should be drawn in Indian ink on Bristol board, stout paper or tracing cloth, not larger than foolscap size and with at least 1-inch margins all round. The use of squared paper should be avoided. All lettering should be inserted lightly in black lead pencil at the appropriate place in the diagram, and will be replaced by type in block-making. All lines in Indian ink should be firmly drawn and sufficiently thick to stand reduction.

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Photographs—Photographs should only be submitted if they convey essential information that cannot be shown in any other way. They should be submitted as glossy prints made to give the maximum detail. Colour photographs can only be accepted when a black-and-white photograph fails to show some vital feature.

Abbreviations—Normality and molarity are generally expressed as decimal fractions (*e.g.*, 0·02 N, 0·375 M). Abbreviational full stops are omitted after the common contractions of metric units (*e.g.*, ml, g, μg, mm) and after °C, °F, μ, Å and other units represented by symbols; litre and metre, when without prefixes, are printed in full.

Abbreviations other than those of recognised units should be avoided in the text; symbols and formulae are not used instead of the names of elements and compounds in the text, but may be used in addition to names when they are necessary to avoid ambiguity, *e.g.*, to specify crystalline composition, as in $CuSO_4.5H_2O$, to show structure or in equations.

Percentage concentrations of solutions should be stated as "per cent. w/w" (alternatively "g per 100 g"), as "per cent. w/v" (alternatively "g per 100 ml") or as "per cent. v/v." Concentrations of solutions of the common acids, however, are often conveniently given as dilutions of the concentrated acids, such as "diluted hydrochloric acid (1 + 4)," which signifies 1 volume of the concentrated acid mixed with 4 volumes of water. This avoids the ambiguity of 1 : 4, which might be equivalent to *either* 1 + 4 *or* 1 + 3.

References—References should be numbered serially in the text by means of superscript figures, *e.g.*, Mackenzie and Mitchell[1] or Furman,[2] and collected in numerical order under "REFERENCES" at the end of the paper. They should be listed, with the authors' initials, in the following form (double-spaced typing)—

1. Mackenzie, R. C., and Mitchell, B. D., *Analyst*, **1962**, **87**, 420.
2. Furman, N. H., *Editor*, "Standard Methods of Chemical Analysis," Sixth Edition, D. Van Nostrand Co. Inc., New York and London, **1962**, Volume **1**, p. **863**.

For books, the edition (if not the first), the publisher and the place and date of publication should be given, followed by the volume or page number, or both if required.

The entry of "personal communications" in the reference list is not justified; full acknowledgement of such unpublished sources should be made in the text or in the acknowledgments at the end of the paper.

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