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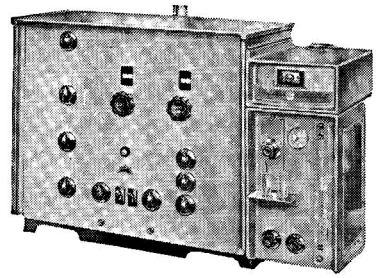
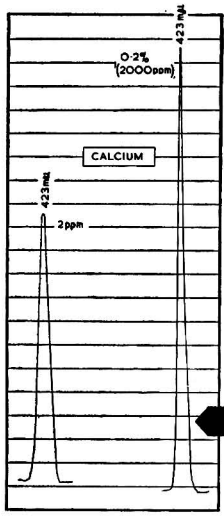
New Fields for Flame Photometry





The application of flame photometry to elements other than those few with particularly strong emission lines (notably Na, K & Li) has been handicapped by the limitations of available instruments. Now the standards of performance achieved by the Unicam SP.900 Flame Spectrophotometer allow the analyst to profit from the ease, speed and accuracy of flame methods in a wide new range of determinations.

Important design features include a silica prism monochromator of high light-gathering power, sensitive detectors and amplifier, and a reliable sample handling system. The instrument is direct reading and is rapid and simple in operation.

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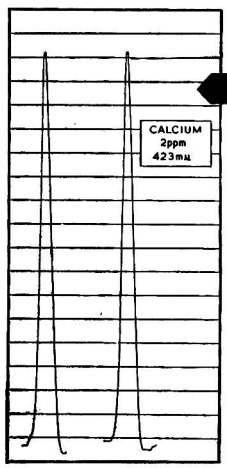
An indication of the scope of the instrument is given by the spectra reproduced on the left, in which Calcium solutions of 2 p.p.m. and 2000 p.p.m. concentrations were run consecutively (after suitable adjustments to the slit width and amplification controls).

Both trace amounts and large concentrations are rapidly and accurately determined by the SP.900.



REPRODUCIBILITY

The high optical quality of the SP.900 and the reliability of its electronic system ensure accurate reproducibility under all operating conditions. The spectra on the left show a repeat run on a 2 p.p.m. Calcium solution.

Accuracy of this order, available for many elements hitherto considered "difficult" for flame photometry, make the instrument an invaluable aid for both research and routine industrial applications.

A series of application sheets for the SP.900 giving details of typical determinations with the instrument, is now in preparation, and the first of these sheets is freely available on request. The following determinations are described:

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THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

AN Ordinary Meeting of the Society was held at 6.30 p.m. on Wednesday, October 1st, 1958, in the Lecture Theatre of The Royal Institution, 21 Albemarle Street, London, W.1. The Chair was taken by the President, Dr. J. H. Hamence, M.Sc., F.R.I.C.

A Report on "The Use of Radiochemical Methods to Investigate the Recovery of Trace Elements from Organic Materials" was given by T. T. Gorsuch, B.Sc., A.R.I.C., with an introduction by R. Spence, C.B., Ph.D., D.Sc., on "Radiochemical Methods."

The work described in this report was the subject matter of the Society's first Research Scholarship and was done at Harwell under the guidance of A. A. Smales, B.Sc., F.R.I.C. The report is shortly to be published in *The Analyst.*

DEATH

WE record with regret the death of

Dattatraya Manjunath Gangolli.

MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 6.30 p.m. on Tuesday, September 16th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

The following four papers from Imperial Chemical Industries (Metals) Ltd., were introduced by the Division Chief Analyst, W. T. Elwell, F.R.I.C.: "The Volumetric Determination of Chloride in Titanium, Zirconium, etc., Using a Polarisation 'Dead-stop' End-point," by D. Price, B.Sc., and F. R. Coe, B.Sc.; "The Determination of Carbon in Metals, Particularly Titanium and Zirconium, with Special Reference to a Simplified Low-pressure Method," by D. F. Wood, B.Sc., A.R.I.C., and D. A. Williams; "The Determination of Lead Styphnate in Priming Compositions Used in Explosives," by H. C. J. Saint, A.R.I.C., and Miss J. Hewson; "The Application of Atomic Absorption Spectrometry in Metallurgical Analysis," by J. A. F. Gidley, B.Sc., A.Inst.P., and J. T. Jones.

Obituary

JAMES RAWSON WALMSLEY

JAMES RAWSON WALMSLEY died in hospital in Manchester on June 4th, 1958. He was 69.

Walmsley was a native of Manchester and spent most of his working life there. He began his scientific career as an apprentice in retail pharmacy, qualifying as a pharmaceutical chemist in 1912. He held a number of positions in retail pharmacy, but after the 1914–18 war entered the wholesale trade with Joseph Brooks & Co. Ltd. In 1921, he was appointed Works Analyst to James Woolley, Sons & Co. Ltd., of Manchester, a position he held until prolonged ill-health compelled him to retire in 1953. After a period of rest, however, his active spirit rebelled against enforced idleness and he spent much time during his last years assisting in the Pharmacy Department of a local hospital. When he died, he had served pharmacy diligently and enthusiastically for over 50 years.

In 1922, he qualified for the Fellowship of the Institute of Chemistry in Branch E, being one of the first to do so under the new regulations instituted a year or two previously.

Walmsley took a keen interest in all aspects of pharmaceutical life. For some years he was a part-time lecturer at the Manchester College of Technology. He was a competent and resourceful analyst. He had an expert knowledge of crude drugs and was a skilful botanist and a keen gardener. Part of his garden at Wilmslow was devoted to the cultivation of medicinal plants. He played an active part in Manchester pharmaceutical circles, serving in 1946–47 as President of the Manchester Pharmaceutical Association and in 1955–56 as Chairman of the Manchester, Salford and District Branch of the Pharmaceutical Society. He was a regular visitor to the Annual Meetings of the British Pharmaceutical Conference and occasionally presented papers to its Science Sessions.

He joined the North of England Section of the Society for Analytical Chemistry in 1924 and did much to foster and encourage its growth. He attended its scientific meetings with unfailing regularity and served on the Committee for several years. He was Honorary Auditor of the Section for a long period prior to 1953, Vice Chairman in 1953–55 and Chairman in 1955–57.

Walmsley was a studious man whose reading embraced a wide field. The historical aspects of a subject always appealed to him. He had an especial love of his native city and a considerable and detailed knowledge of its history back to Roman times. For many years he was a member of the Manchester Literary and Philosophical Society and the Manchester Microscopical Society. He loved the open air and the English and Scottish countryside where his knowledge of botany and natural history provided added interest to his excursions.

A quiet unassuming man, with a quiet sense of humour, a loyal colleague and a "guide, philosopher and friend" to those less experienced than himself, Walmsley pursued his profession and his many interests with a lively zest. He was a sociable and companionable man, never happier than in the society of his fellow analysts, and he leaves behind him in our Society and in pharmacy a wide circle of friends who will long remember him with affection and think of his passing with regret.

Mrs. Walmsley predeceased him by some years, and he left no family.

G. J. W. FERREY

The Determination of Trace Amounts of Aluminium in Cast Iron

BY R. C. ROONEY

(The British Cast Iron Research Association, Bordesley Hall, Alvechurch, Birmingham)

A method is described for determining trace amounts of aluminium in cast iron. After preliminary separation of the major constituents by extraction as their diethyldithiocarbamate complexes into chloroform, the aluminium is selectively extracted as cupferrate at pH 4·5. The final determination is made by the polarographic procedure of Willard and Dean.

The determination of the acid-insoluble aluminium fraction is described, and the purity of reagents is discussed. The method is also applicable to steel.

RECENT work at the British Cast Iron Research Association and elsewhere has shown that small amounts of aluminium can have marked effects on the properties of cast iron, particularly with regard to pinholing,[1] inoculation[2] and annealability.[3,4,5] In order to investigate these effects, it has become necessary to develop analytical methods for determining aluminium at concentrations well below 0·01 per cent. It was also considered desirable to develop a method to cover the range 0·01 to 0·2 per cent.; this latter figure represents the useful lower limit of the fluoride volumetric method previously developed in these laboratories.[6]

Colorimetric procedures for iron and steel, in which lake-forming reagents, such as Eriochrome cyanine and aluminon, are used have been reported,[7,8,9] but these reagents have disadvantages. Close control of conditions is necessary if reproducible results are to be obtained, and the reagents are subject to interferences, especially from iron.

Measurement of the colour of aluminium 8-hydroxyquinolate in chloroform has been used,[10,11] but this reagent is again subject to interference by iron and many other constituents

of cast iron. Other methods suggested include turbidimetric measurements with cupferron as reagent[12,13] and fluorimetric measurements with reagents such as Pontachrome blue-black R.[14]

The polarographic method of Willard and Dean[15] is very successful for steels containing more aluminium than titanium and vanadium, but in cast iron these elements are usually present in far greater amounts than the aluminium. The mercury-cathode separation used by these workers does not separate aluminium from titanium and vanadium, and, when microgram amounts of aluminium are involved, there is interference from the residual amounts of nickel, chromium, lead, etc. in the electrolyte. The chromatographic separation used by Bishop[16] suffers from the same defects, as separation from titanium, vanadium, lead, cerium, zirconium, chromium, nickel, cobalt and several other possible micro and semi-micro constituents of cast iron is either not effected by this procedure or only partly effected. The small-scale mercury-cathode electrolysis recommended by Bishop after elution of the aluminium is effective for removing some of these elements, but not all.

It is obvious that, in order to determine aluminium satisfactorily by any of the colorimetric procedures at the microgram level, it must be completely separated from all traces of the other constituents of the cast iron. In practice, it was found to be impossible to obtain the aluminium completely free from other metals, especially in a laboratory in which other analysis was being carried out. It was found that air-borne contamination of the solutions with microgram amounts of iron was particularly difficult to prevent, and led to the presence of iron in the final solutions, although it could be shown that, at the intermediate stages, the solutions were completely iron-free.

The polarographic procedure is more tolerant to many metals in small amounts, and, if a polarograph with good resolution is used, interfering elements, such as iron, titanium and nickel, can be tolerated so long as their concentration can be reduced below that of the aluminium. Because of this, the polarographic method of determination was used; a cathode-ray polarograph gave the necessary sensitivity and resolution.

Experimental

Polarography—

The polarographic determination of aluminium with Solochrome violet RS was investigated by using the conditions recommended by Willard and Dean. When 20·0 ml of a 0·05 per cent. aqueous solution of Solochrome violet RS and a final volume of 50 ml were used, a straight-line graph was obtained over the range 50 to 200 μg of aluminium. At 40 μg, measurement of the aluminium peak became somewhat difficult, owing to the previous reduction of the dye-stuff. A second graph was plotted, for which 5·0 ml of dye solution were used, and it satisfactorily covered the range 10 to 60 μg; a third graph, for which 1·0 ml of reagent was used, covered the range 1 to 15 μg. The blank value of the cell reagents was originally 4 μg, but, after a considerable amount of work (see "Purity of Reagents," p. 548) this was reduced to 1 μg; work below this level was deferred until better reagents are available. These graphs had different slopes, the factors being 1 μA $\equiv$ 24, 14 and 12 μg, respectively. This effect is ascribed to increases in the viscosity leading to lower diffusion coefficients in the solutions containing large amounts of dye-stuff. The range of aluminium that could be determined was further extended by using one-fifth of the volume of all reagents in a final volume of 10 ml. These conditions were used in conjunction with the graph covering the range 1 to 15 μg to give a range of 0·2 to 3·0 μg. Because of the difficulties that were encountered with regard to blank values, this range was rarely used.

The effect of various elements under the conditions used for the polarographic determination was next examined. By using 100 μg of each element and 20 ml of dye solution, most of the elements likely to be present with the aluminium were examined. Interference was found to be caused by ferric and ferrous iron, titanium, vanadium, nickel, cobalt, zirconium and chromium. This agrees with the work of Perkins and Reynolds,[17] who also found interferences from large amounts of cadmium, molybdenum, thorium, antimony, lead, copper and tin. As many of these elements are likely to be present in cast iron at concentrations equal to or greater than that of the aluminium, any separation procedure must remove them.

Separation of aluminium—

It became obvious during the early part of this work that the separation procedure most likely to be useful was one in which the smallest amounts of reagents were used. Great

difficulty was encountered with aluminium in the reagents, aluminium in filter-paper, aluminium leached from the glassware and many other sources of contamination.

Rosotte's method[13] was used as a starting point for the work, as she had already reported the interference of residual iron after separation at a mercury cathode, together with that of titanium and vanadium, and had overcome this. No mention was made, however, of residual amounts of elements, such as manganese and chromium, which are difficult to deposit completely in mercury. Rosotte removed the residual iron, together with titanium and vanadium, by extraction of the cupferrates at pH 0·3, and, after destroying the excess of cupferron, adjusted the pH to 3·9 and added more cupferron. The turbidity caused by the finely divided aluminium cupferrate was used to determine its concentration, but it seemed preferable to extract this aluminium cupferrate in order to use the more satisfactory method of determination.

First, the pH conditions for extraction were examined by using 250 μg of aluminium and 1·0 ml of a 1 per cent. solution of cupferron. The results, corrected for the blank value, were as follows—

pH	0·5	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0
Aluminium found, μg	Nil	0·35	155	196	240	246	228	209	10·7
Extraction, %	Nil	0·14	62	79	98	99	91	84	4

From these results it is apparent that a preliminary extraction with cupferron would be satisfactory, provided that the pH is kept below 1·0, and that, for efficient extraction of the aluminium, the pH must lie between 4 and 5. This is readily achieved by the use of an acetate - acid buffer system.

Under these conditions, extractions were made over a range of aluminium concentrations (the extractions of 0·1 and 1·0 μg were made at a later stage with lower blank values). The results, corrected for the blank values, were as follows—

Aluminium added, μg	0·1	0·1	1·0	1·0	10·0	50	100	200
Aluminium found, μg	0·1	0·1	1·2	0·96	9·8	51	98	205
Recovery, %	100	100	120	96	98	102	98	103

The recoveries were considered to be satisfactory. Extraction of 10 μg of aluminium was also successfully accomplished in the presence of 10 mg of phosphorus pentoxide; phosphate in solutions of high-phosphorus irons will therefore not interfere.

As 1 μg of aluminium can be determined readily, it was considered likely that aluminium contents of 0·001 to 0·2 per cent. could be determined easily by using a 0·1-g sample of iron; this corresponds to the range of the graphs, 1·0 to 200 μg. For cast irons containing very little nickel, chromium or cobalt, no preliminary separation of these elements should be necessary, so that a direct cupferron separation of iron, titanium, vanadium, etc., could be made, followed by adjustment of pH and extraction of the aluminium.

This procedure was used and a blank value of 14 μg was obtained, equivalent to 0·014 per cent. The procedure was applied to a further series of samples after a preliminary separation at a mercury cathode; a blank value of 11 μg was obtained. It became apparent that an investigation of the purity of the reagents was necessary.

Purity of reagents—

The reagents used in the experimental work were examined by various concentration and extraction procedures in order to determine their aluminium contents; some alternative reagents were also examined. The results are shown in Table I.

It was found that ashless filter-papers could contribute 2 to 3 μg of aluminium; silica and graphite residues were therefore removed by centrifugation in all the subsequent work. Samples of lead-free perchloric acid, which had been redistilled, were obtained from the British Drug Houses Limited and from Hopkin and Williams Limited. The aluminium contents were found to be of the order of 0·05 to 0·1 p.p.m., which indicates the difficulty associated with the further purification of reagents.

It was decided to use lead-free acids when possible and to attempt to purify the cupferron and sodium acetate. Many methods for both reagents were used, including selective solvent extraction with a number of reagents and solvents, ion exchange under various conditions with both anion and cation-exchange resins, recrystallisation and synthesis of the reagents under closely controlled conditions. However, the aluminium content of the reagents was

never significantly decreased, and it is suggested that this is probably due to the aluminium in these neutral reagents being present as aged aluminium hydroxide, which would be comparatively unreactive.

TABLE I

ALUMINIUM CONTENT OF REAGENTS

Reagent	Grade	Aluminium content, p.p.m.
Perchloric acid	AnalaR*	3·0
Sulphuric acid	AnalaR*	1·0
Hydrochloric acid	AnalaR*	0·65
Nitric acid	AnalaR*	0·83
Hydrogen peroxide, 100-volume	AnalaR*	0·032
Sodium acetate	AnalaR*	0·088
Cupferron	AnalaR*	4·4
Sodium diethyldithiocarbamate	AnalaR*	<0·001
Chloroform	AnalaR*	<0·001
Perchloric acid	"Lead free, for foodstuffs analysis"†	0·25
Hydrochloric acid	"Lead free, for foodstuffs analysis"†	0·007
Nitric acid	"Lead free, for foodstuffs analysis"†	0·034

* Samples of reagents of similar grade were examined and found to have similar aluminium contents.
† When aged in glass bottles, the aluminium content rises appreciably.

In view of the high aluminium content of cupferron, it was decided to use sodium diethyldithiocarbamate for the preliminary separation of iron. This would also remove copper, nickel, cobalt, manganese and vanadium,[18] and recent work in our laboratory has shown that the bulk of the titanium is also extracted.[19] Any residual titanium will be detected and can be separated. No more attempts were made to purify sodium acetate further; each batch used was tested for aluminium and any very impure batches were rejected.

APPARATUS—

Oelschläger[20] reported that microgram amounts of aluminium could be leached from glassware by a variety of reagents. This work was confirmed, and it was found that a blank value of 6 μg when glass apparatus was used could be reduced to 1·8 μg if silica or polythene apparatus was substituted whenever possible. Silica and polythene apparatus was therefore used when possible in the subsequent work.

APPLICATION OF THE METHOD TO CAST IRON

ACID-SOLUBLE ALUMINIUM—

Methods were devised for determining aluminium in cast iron and were checked by investigating the recovery of aluminium added to samples of pure iron. The results are shown in Table II. An outline of the procedures used, which are described fully under "Method," p. 550, is as follows—

Procedure A—Iron extracted as diethyldithiocarbamate from a 0·1-g sample.
Blank value = 2·1 μg ≡ 0·0021 per cent. of aluminium.
Procedure B—Iron extracted with *iso*butyl acetate from a 5-g sample.
Blank value = 22 μg ≡ 0·00044 per cent. of aluminium.
Procedure C—Electrolysis - dissolution procedure on a 5-g sample.
Blank value = 1·2 μg ≡ 0·000024 per cent. of aluminium.

It is apparent that the useful lower limit of the method is set by the blank value. In our laboratory, for a figure to be regarded as reliable, it must not be lower after correction than the blank value alone, *i.e.*, the "signal-to-noise" ratio must not be less than 1 to 1. In order to obtain the lowest possible blank value for the lowest aluminium contents, the sample must be dissolved in a very small amount of acid and the bulk of the iron separated by using a minimum of reagents. This problem was solved in an elegant manner by Chirnside, Cluley and Proffit[21] in their method for the determination of boron in nickel strip. The solid sample is used as anode in a mercury-cathode electrolysis cell, a small amount of acid is added and dissolution and deposition proceed simultaneously. By using a high current density and feeding the sample into the electrolyte as it dissolves, 5 g of iron can be dissolved

in about 2 hours in only 1·0 ml of perchloric acid. The extraction of the elements remaining in solution (mainly titanium and vanadium) also requires small amounts of reagents.

TABLE II

RECOVERY OF ALUMINIUM ADDED TO SAMPLES OF PURE IRON

Procedure	Basis material	Aluminium added, μg	Aluminium found (corrected for blank value), μg	Recovery, %
A	Commercially pure iron	Nil	0·9*	—
		10	9·8	98
		50	52	104
		100	105	105
		200	199	99·5
B	Spectrographically pure iron ..	50	49	98
		100	101	101
		200	200	100
C	Spectrographically pure iron ..	1·0	0·98	98
		5·0	5·0	100
		10	9·9	99
		50	50	100

* This figure is lower than the blank value and should be neglected.

If solid samples or the electrolysis apparatus are not available, the lower limit can be extended below 0·002 to about 0·0004 per cent. by using a 5-g sample and extracting the iron with *iso*butyl acetate. The 11 per cent. loss of aluminium reported by Werz and Neuberger,[22] who extracted the iron with diethyl ether, is not confirmed, and it is suggested that this discrepancy is caused by the relatively high solubility of diethyl ether in hydrochloric acid compared with the almost complete insolubility of *iso*butyl acetate. For large numbers of samples with aluminium contents greater than 0·0004 per cent., procedure *B* is often more convenient than procedure *C*.

The interfering elements left in solution in all procedures are most likely to be titanium, cerium, zirconium, etc., if present, and chromium. Of these, titanium, cerium, etc., will be extracted quantitatively with the aluminium as cupferrates, and, if the pH is greater than 4·2 to 4·3, some chromium may also be extracted. The presence of most of these elements with the aluminium will be obvious, however, and they can be removed fairly simply.

ACID-INSOLUBLE ALUMINIUM—

Because the aluminium present can be partly extracted from filter-papers by acid solutions, it was decided to determine the acid-insoluble fraction on a different sample. This would allow the use of a large sample weight, as the aluminium in the acid used to dissolve the sample would pass through the filter-paper and be discarded; the large sample weight would minimise the effect of the blank values contributed by reagents such as sodium carbonate and hydrofluoric and sulphuric acids, which are difficult to purify.

It has been found with several samples that the results for acid-insoluble aluminium are erratic; one particularly bad example gave results ranging from 0·00016 to 0·00052 per cent. As other samples gave reproducible results, it is thought possible that there is a tendency to marked heterogeneity in the distribution of the insoluble aluminium throughout some samples.

The methods have been applied to a number of samples; representative results are shown in Table III. It is considered that these results, with the exception of the insoluble fractions in the samples of grey iron and iron containing 4 per cent. of chromium, show satisfactory reproducibility.

METHOD

APPARATUS—

All beakers should be of silica, with silica or polythene covers. Normal volumetric glassware is satisfactory, but solutions should not be allowed to remain in contact with it for longer than necessary; pipettes should not be left standing in bottles of reagents. Polythene storage bottles should be filled with concentrated hydrochloric acid and set aside for 48 hours; they should then be washed well with water before use.

TABLE III

DETERMINATION OF ACID-SOLUBLE AND ACID-INSOLUBLE ALUMINIUM IN SAMPLES OF IRON

Sample	Procedure	Acid-soluble aluminium found, %	Acid-insoluble aluminium found, %
Pig iron	*A*	0·010, 0·011, 0·010 0·0022, 0·0022, 0·0020 0·0075, 0·0080, 0·0082	0·0022, 0·0022 0·00076, 0·00078 0·0013, 0·0012
Grey iron	*B*	0·00092, 0·00096, 0·00095	0·00016, 0·00032, 0·00018, 0·00052, 0·00040
Iron containing 4 per cent. of chromium	*C*	0·00038, 0·00040, 0·00038	0·00045, 0·00072, 0·00056
Spectrographically pure iron	*C*	0·00003, 0·00004, 0·00003	Not determined

For polarography, a cathode-ray polarograph was used to attain maximum sensitivity. The utility of the method will be limited by the instrument available.

For procedure *C*, a 50-ml tall platinum crucible is recommended for the electrolysis, but satisfactory results can be obtained by using pure nickel or stainless-steel crucibles, provided that they do not give rise to high blank values.

REAGENTS—

Perchloric acid, 5 N—Dilute 500 ml of perchloric acid, sp.gr. 1·54, to 1 litre with distilled water (see "Water" below). For aluminium contents greater than about 0·01 per cent., AnalaR or equivalent grade perchloric acid should be satisfactory; for below 0·01 per cent. of aluminium, redistilled or "lead free for foodstuffs analysis" perchloric acid should be used. It is advisable to dilute the lead-free acid as soon as received and to store it in a polythene bottle.

Hydrochloric acid, sp.gr. 1·18—For aluminium contents greater than about 0·01 per cent., AnalaR or equivalent grade is satisfactory. For lower aluminium contents, the "lead free for foodstuffs analysis" acid should be used, preferably stored in polythene.

Nitric acid, sp.gr. 1·42.—Use the grades of reagent as described for hydrochloric acid, but do not store in polythene.

Chloroform—AnalaR or equivalent grade is satisfactory.

Acetic acid, glacial—AnalaR or equivalent grade is usually satisfactory. For very low aluminium contents, it may be necessary to redistil the acid.

Sodium acetate solution, 2 M—Dissolve 272 g of the purest hydrated sodium acetate available in water and dilute to 1 litre. Distilled water must be used for this solution.

Sodium diethyldithiocarbamate solution, 20 *per cent.*—Dissolve 20 g of AnalaR or equivalent grade sodium diethyldithiocarbamate in water and dilute to 100 ml. This solution must be freshly prepared.

Cupferron solution, 1 *per cent.*—Dissolve 1 g of the purest available cupferron in 100 ml of water and spin in a centrifuge at 10-cm radius and 2000 r.p.m. for 3 minutes. Use the supernatant liquid. This solution must be freshly prepared.

iso*Butyl acetate*—Analytical-reagent grade is usually satisfactory. If high blank values are obtained, the reagent can be purified by shaking it for about 10 minutes with half its own volume of 5 *N* hydrochloric acid.

Solochrome violet RS solution, 0·05 *per cent.*—Dissolve 0·5 g of the pure dye-stuff in 1 litre of distilled water and store in a polythene bottle.

Water—For the earlier stages of the method, distilled or de-ionised water is satisfactory, but the solutions used in the base electrolyte must be made up with *distilled* water. De-ionised water can give rise to spurious polarographic waves and false figures.[23]

Standard aluminium solution A—Dissolve exactly 2·5 g of high-purity aluminium in hydrochloric acid, add 50 ml of perchloric acid and evaporate to the appearance of fumes. Cool, and dilute to 500 ml. This solution is stable indefinitely.

1 ml ≡ 0·005 g of aluminium.

Standard aluminium solution B—Dilute 2·0 ml of solution A to 1 litre with redistilled water. This solution should be freshly prepared as required.

1 ml ≡ 10 μg of aluminium.

Standard aluminium solution C—Dilute 20 ml of solution B to 200 ml with water. This solution should be freshly prepared as required.

1 ml ≡ 1 μg of aluminium.

PREPARATION OF CALIBRATION GRAPHS—

Graph for 40 to 200 μg of aluminium—In a series of 50-ml calibrated flasks place 0, 4, 8, 12, 16 and 20-ml portions of standard aluminium solution B, and add 1 drop of methyl red indicator solution. Make just alkaline by adding *N* sodium hydroxide, and then add 1·0 ml of 5 *N* perchloric acid. Add 5·0 ml of 2 *M* sodium acetate solution, 20 ml of 0·05 per cent. Solochrome violet RS solution and dilute to the mark. Immerse the flasks in a water bath at 55° to 70° C for 5 minutes, and then cool and record polarograms between −0·50 and −0·85 volt against the internal pool anode; the aluminium peak occurs at about −0·72 volt. Plot a graph of microamperes against micrograms of aluminium per 50 ml, subtracting the blank value from all readings in order to make the line pass through the origin.

Graph for 10 to 60 μg of aluminium—Proceed as for the preparation of the graph for 40 to 200 μg of aluminium, but use 0, 1, 2, 3, 4, 5 and 6-ml portions of standard aluminium solution B and 5·0 ml of Solochrome violet RS solution. Immediately after diluting to the mark, transfer the solutions to 50-ml stoppered polythene bottles for the period of heating.

Graph for 1 to 15 μg of aluminium—Proceed as for the preparation of the graph for 10 to 60 μg of aluminium, but use 0, 1, 3, 5, 7, 10, 12 and 15-ml portions of standard aluminium solution C and 1·0 ml of Solochrome violet RS solution. These solutions will need to be de-oxygenated very thoroughly.

PROCEDURE FOR DETERMINING ACID-SOLUBLE ALUMINIUM—

A. Aluminium contents from 0·002 to 0·2 per cent.—Weigh 1·0 g of sample into a 150-ml squat beaker and dissolve without heating in 20 ml of diluted hydrochloric acid (1 + 1). When dissolved, cool, and dilute to the mark in a 100-ml calibrated flask. Transfer immediately to a polythene centrifuge tube and spin in a centrifuge at 10-cm radius and 2000 r.p.m. for 2 to 3 minutes. By pipette, place 10 ml of the supernatant liquid (≡ 0·10 g of sample) in a 150-ml conical separating funnel and add 5·0 ml of acetic acid, 10 ml of sodium acetate solution and 20 ml of sodium diethyldithiocarbamate solution. Shake the separating funnel for 10 to 20 seconds, add 30 ml of chloroform, and shake vigorously for 30 seconds. Allow the two layers to separate, rinse the stopper and neck of the funnel with chloroform from a polythene wash-bottle in order to remove particles of precipitate adhering to them, and run off the chloroform layer. Add a further 10 ml of chloroform, shake again, and allow the layers to separate. Add a few drops of sodium diethyldithiocarbamate solution to test for completeness of precipitation; there should be a white precipitate. If the precipitate is coloured, add 5 ml of sodium diethyldithiocarbamate solution, and shake to extract the precipitate in the chloroform layer. Again test for completeness of precipitation; repeat until a white precipitate is obtained when sodium diethyldithiocarbamate solution is added. Shake, allow the two layers to separate, and then run off the chloroform layer. Extract the aqueous layer with 10-ml portions of chloroform, washing the neck and stopper of the funnel with chloroform after each extraction until the chloroform layer is perfectly colourless (25 ml of sodium diethyldithiocarbamate solution and 50 to 60 ml of chloroform should be sufficient). Discard the chloroform extracts and wash the stem of the funnel with chloroform, removing any stubborn particles with a "spill" of filter-paper.

To the aqueous solution in the separating funnel, add 1·0 ml of cupferron solution and set aside for 1 to 2 minutes. Add 15 ml of chloroform, shake vigorously for 30 seconds, and allow the two layers to separate. Note whether the chloroform extract is perfectly colourless or coloured. Run the chloroform layer into a 50-ml beaker, and repeat the extraction with 10 and then 5 ml of chloroform, adding these extracts to the 50-ml beaker.

Evaporate the chloroform extracts to dryness and add 1·0 ml of nitric acid and 2·0 ml of 5 *N* perchloric acid. Keep the beaker covered with a well fitting lid in order to minimise loss of perchloric acid, and evaporate to fumes of perchloric acid; continue heating until all organic matter has been destroyed. If the chloroform extract is green owing to the co-extraction of a small amount of chromium from high-chromium irons, the residue in the beaker will probably be orange at this stage, owing to the oxidation of chromium. If chromium is present, add a further 2·0 ml of 5 *N* perchloric acid, evaporate to the appearance of fumes, and remove the lid. Add 0·5 to 1·0 ml of hydrochloric acid to volatilise the

chromium as chromyl chloride, replace the lid, and again evaporate to the appearance of fumes. If sufficient chromium is left to colour the residue, add a further 0·5 ml of hydrochloric acid. Continue this procedure, adding more perchloric acid if necessary to maintain the volume, until no orange colour is obtained on further heating to fumes. One addition of hydrochloric acid is usually sufficient. When all organic matter and chromium have been removed, remove the lid and evaporate to dryness. If the chloroform extract is colourless or pale green, proceed as follows.

Dissolve the residue in 1·0 ml of 5 *N* perchloric acid and transfer the solution to a 50-ml calibrated flask. Add 5·0 ml of 2 *M* sodium acetate and 1·0, 5·0 or 20·0 ml of Solochrome violet RS solution, according to the amount of aluminium present. Dilute to the mark with distilled water, and, if 1·0 or 5·0 ml of dye solution were used, transfer the solution to a screw-top polythene bottle. Complete the determination as for the preparation of the calibration graphs and read the aluminium contents corresponding to the step or peak heights from the appropriate curve.

If the chloroform extract is yellow or brown, owing to the presence of titanium or iron, proceed as follows.

Dissolve the residue in 1·0 ml of 5 *N* perchloric acid and transfer the solution to a 150-ml conical separating funnel. Adjust the volume to 50 to 60 ml and add 1·0 ml of cupferron solution. Add 10 ml of chloroform, shake for 30 seconds, and then allow the two layers to separate. Run off the chloroform layer, and wash the aqueous layer with a further 10 ml of chloroform. Continue to shake with 10-ml portions of chloroform until the extract is colourless; two 10-ml portions are usually sufficient. Add 10 ml of 2 *M* sodium acetate solution, shake, and add 1·0 ml of cupferron solution. Extract the aluminium as before, and complete the determination as described. A blank determination must be carried out by treating the reagents alone in the manner described for the sample. If a batch of samples is processed, one blank determination is sufficient, but all samples must then be processed similarly, even though some may contain no chromium or titanium. Unless these samples are processed identically with any that do contain chromium or titanium, and with the blank determination, the correction applied for the blank value will no longer be accurate.

B. Aluminium contents from 0·0004 *to* 0·004 *per cent. in plain cast irons only*—Weigh 5 g of sample into a 400-ml beaker and dissolve it in 40 ml of hydrochloric acid and 10 ml of nitric acid without heating. When dissolved, cool, and transfer the solution to a centrifuge tube, washing with concentrated hydrochloric acid from a polythene wash-bottle. Spin in a centrifuge at 10-cm radius and 2000 r.p.m. for 3 minutes, and then transfer the supernatant liquid to a 250-ml conical separating funnel. Add 150 ml of *iso*butyl acetate, and shake for 30 seconds. Allow the two layers to separate and run the lower (acid) layer into a 150-ml beaker. Evaporate to dryness, add 5·0 ml of nitric acid and 4·0 ml of 5 *N* perchloric acid, and then evaporate to fumes of perchloric acid. When all organic matter has been destroyed, cool, and transfer the solution to a 150-ml separating funnel. Add 15 ml of 2 *M* sodium acetate and 20 ml of 20 per cent. sodium diethyldithiocarbamate solution. Extract the interfering elements and then the aluminium, and complete the determination as for procedure *A*.

C. Aluminium contents less than 0·0004 *per cent. in plain cast irons or less than* 0·005 *per cent. in alloy cast iron*—Solid samples must be used for this determination and they should be pencil shaped. Weigh the sample and calculate the approximate length that will correspond to the desired weight of sample. Set up a cell as described by Chirnside, Cluley and Proffit,[21] with a 50-ml platinum crucible containing a 20-ml pool of mercury. The crucible is connected to the cathode lead, and 20 ml of water and 2·0 ml of 5 *N* perchloric acid are added. Connect the sample to the anode lead by means of a crocodile clip, and electrolyse at 3 to 5 amperes. Lower the sample into the solution as it dissolves, and maintain the volume of electrolyte at about 20 ml by the addition of water. It is advantageous to cool the crucible in running water if possible and to stir the mercury pool with a bone spatula from time to time. When the calculated length of sample has dissolved, remove, wash and dry the sample, and re-weigh it in order to obtain the weight dissolved. With a flat spiral of platinum wire as anode, continue to electrolyse until the electrolyte gives no test for iron. Disconnect the leads and decant the solution from the mercury into a polythene centrifuge tube, washing with water. If this operation is carried out quickly, the amount of iron that will re-dissolve is very small. Spin in a centrifuge at 10-cm radius and 2000 r.p.m. for 2

minutes in order to remove any insoluble residue of silica, graphite, etc., and transfer the supernatant liquid to a 150-ml squat beaker. Add 2 or 3 drops of 100-volume hydrogen peroxide, and boil for a few minutes to destroy excess of peroxide. Cool, and transfer to a 150-ml conical separating funnel. Add 1·0 ml of 1 per cent. cupferron solution, shake, and extract the precipitate in 10 ml of chloroform. Add a further 1·0 ml of cupferron solution, and, if a coloured precipitate forms, shake once more to extract it in the chloroform layer. Continue until the precipitate obtained is white; this should not require more than 3 or 4 ml. Shake for 30 seconds, allow the two layers to separate, and run off the chloroform layer. Extract the aqueous layer with further 10-ml portions of chloroform until the chloroform layer is colourless; add 20 ml of 2 *M* sodium acetate and then 1 ml of 1 per cent. cupferron solution. Extract the aluminium and complete the determination as for procedure *A*.

PROCEDURE FOR DETERMINING ACID-INSOLUBLE ALUMINIUM—

Weigh a 10-g sample into a 400-ml beaker and dissolve it in 100 ml of diluted hydrochloric acid (1 + 1). Boil, and filter through a No. 541 filter-paper of the smallest convenient size, washing well with hot dilute hydrochloric acid (1 + 19). Dry and ignite in a platinum crucible at 700° to 800° C until all carbonaceous matter has been destroyed.

Treat the residue with 2 or 3 ml of hydrofluoric acid and 10 drops of dilute sulphuric acid (1 + 4), and then heat on a radiation bath until all the silica has been volatilised and white fumes of sulphur trioxide appear. Evaporate to dryness, but do not bake. Add a further 10 drops of dilute sulphuric acid (1 + 4) and again evaporate to dryness.

Fuse the residue with 1·0 g of sodium carbonate and leach the melt with hot water. Add 5 ml of hydrochloric acid, 1 or 2 drops of nitric acid and evaporate just to dryness. Dissolve the residue in 1·0 ml of hydrochloric acid, and transfer the solution to a 150-ml separating funnel. Add 5·0 ml of acetic acid and 10 ml of 2 *M* sodium acetate, shake, and then add 10 ml of sodium diethyldithiocarbamate solution. Complete the determination as for procedure *A* (see Note). A blank determination must be carried out on the reagents, including the filter-paper and the hydrochloric acid used to dissolve the sample.

NOTE—If the acid-insoluble aluminium content is in excess of 0·002 per cent., 1·0 ml of cupferron solution may be insufficient for precipitation. This will be shown by the formation of a coagulated precipitate of aluminium cupferrate rather than a milky suspension; the most satisfactory procedure then is to extract the aluminium in the chloroform layer and add a further 1·0 ml of cupferron solution. If a precipitate forms, extract this in the chloroform and continue until no further precipitate forms. The determination should then be carried out on an aliquot of the final solution containing less than 200 μg of aluminium; the size of aliquot to be taken can be approximately determined from the relationship between cupferron and aluminium, *i.e.*, 1 ml of 1 per cent. cupferron solution is approximately equivalent to 500 μg of aluminium.

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The Determination of Chromium by a Solvent-extraction Method

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A method is described for the determination of small amounts of chromium in the presence of similar amounts of iron and nickel in solutions 0·04 *M* in uranium and 0·005 *M* in copper. The chromium is oxidised to chromate with ammonium hexanitratocerate in hot acid solution. The chromate is extracted with *iso*butyl methyl ketone from a solution *M* with respect to hydrochloric acid at a temperature of $\leqslant 10°$ C. The chromate is then extracted from the *iso*butyl methyl ketone by two successive water washes and is determined colorimetrically with diphenylcarbazide. In the presence of 100 μg each of nickel and iron, chromium was determined in the range 10 to 100 μg with a mean recovery of 100·3 per cent. and a standard deviation of $\pm$0·8 per cent.

A METHOD was required for determining 1 to 100 μg of chromium in solutions 0·04 *M* in uranium, 0·005 *M* in copper and containing 1 to 100 μg each of iron and nickel. Chromium, iron and nickel arise from corrosion of a stainless-steel containing vessel at high temperature and pressure.

The colorimetric determination of chromium with diphenylcarbazide after oxidation to chromate is the most sensitive method known. The critical stage in this procedure is the oxidation of chromium to chromate. Several methods have been described for this oxidation and they are summarised in Table I. Some were tried in this laboratory, but, at the low concentrations of chromium involved, complete oxidation was evidently not achieved, the results being neither reproducible nor in agreement with those for pure dichromate solutions.

TABLE I

METHODS FOR THE OXIDATION OF TERVALENT CHROMIUM

Oxidant	Medium	Method for destroying excess of oxidant	Results
Ammonium persulphate	Sulphuric acid	Boiling	Not reproducible
	Sulphuric acid and a trace of silver nitrate	Boiling	Not reproducible
	Orthophosphoric acid	Boiling	Thorium phosphate precipitated
Potassium permanganate	Sulphuric acid, 0·5 *N*	Addition of sodium azide or hydrochloric acid	Not reproducible
Potassium bromate	Acid solution	Decomposition with hydrochloric acid	Not attempted
Perchloric acid	—	Evaporation until fumes are evolved	Not attempted
Ceric sulphate or ammonium hexanitratocerate	Hot acid solution	Addition of sodium azide or sodium nitrite	Complete oxidation and good reproducibility

Willard and Young[1] describe a volumetric method for chromium in which ceric sulphate in acid solution at a temperature of 100° C is used as oxidant. Excess of ceric ions may be destroyed with sodium azide or sodium nitrite, the former being preferred.

The literature contains conflicting reports about the elements that interfere in the chromate - diphenylcarbazide reaction. A variety of solvent systems are suggested for preparing diphenylcarbazide reagent solution. Urone[2] studied this problem and found that acetone and ethyl acetate give the most stable reagent solutions.

Bryan and Dean[3] describe the use of *iso*butyl methyl ketone (hexone) as a selective solvent for chromate from *M* hydrochloric acid before a flame-photometric determination of chromium. The selective action of hexone for chromate is fully described by Weinhardt and Hixson.[4]

It was decided, therefore, to utilise the hexone extraction of chromium, after oxidation to chromate by ceric solutions, for the separation from interfering elements before a colorimetric determination with diphenylcarbazide.

Experimental

Ceric oxidation—

Aliquots of chromium potassium sulphate solution containing 10 to 100 μg of chromium^{III} were placed in 40·0-ml centrifuge tubes. Two millilitres of 4 *N* sulphuric acid and 2·0 ml of approximately 0·02 *N* ammonium hexanitratocerate were added. These solutions were diluted to about 15·0 ml and the tubes were immersed in boiling water for 25 minutes. They were then removed and cooled to $<10°$ C. Sodium azide solution (2·0 per cent.) was added dropwise with swirling to destroy the excess of ceric ions. The solutions were then transferred to 100-ml calibrated flasks containing 3·0 ml of 4 *N* sulphuric acid and diluted to approximately 90 ml. Two millilitres of a 1·0 per cent. solution of diphenylcarbazide in acetone were added to each flask and the solutions were made up to the mark. After they had been set aside for 5 minutes, the optical density of each solution was measured in 2-cm cells with a Spekker absorptiometer, Ilford No. 605 filters being used.

The procedure was then repeated with aliquots of potassium dichromate solution over the range 10 to 100 μg of chromium. The results agreed with those for the chromium potassium sulphate solutions and also with those found for potassium dichromate solutions in which the ceric oxidation had been omitted.

Solvent extraction—

Aliquots of potassium dichromate solution containing between 10 and 100 μg of chromium^{VI} were taken and the ceric oxidation procedure was repeated as far as the cooling stage, and then 8·0 ml of 4 *M* hydrochloric acid were added while the solutions were cooling. Each solution was then transferred to a 100-ml graduated separating funnel and was diluted to 32 ml with water, which made each solution *M* with respect to hydrochloric acid. Twenty millilitres of hexone saturated with *M* hydrochloric acid were then added to each. After they had been shaken for 1 minute, the layers were allowed to separate and the aqueous layers were run off and discarded. The hexone layers were then washed twice with 20·0-ml portions of water and the washings were run into 100-ml calibrated flasks containing 5·0 ml of 4 *N* sulphuric acid. The diphenylcarbazide colours were developed and the optical densities were measured in the same way as before.

The procedure was repeated with a solution of chromium potassium sulphate; the results were in good agreement with those for the potassium dichromate solution. About 97 per cent. of the chromium is recovered by the extraction, but the loss can be compensated for by incorporating the extraction in the calibration procedure. The mean temperature of the solutions during oxidation was 93° C and before extraction it was $<10°$ C.

Effect of interfering ions—

Cations—Suitable amounts of elements that might interfere in the determination were added, singly and together, to solutions containing 50 μg of chromium^{VI}. Colours were developed with diphenylcarbazide and the optical densities were measured with a Spekker absorptiometer. It was found that, when the solutions contained copper or iron, the colour faded rapidly, but, in the other solutions, the colour was stable for at least 2 hours. The results in Table II show that uranium, thorium and nickel do not interfere, but iron and copper cause low results. Identical results were obtained from solutions of tervalent chromium, which were oxidised to the sexavalent state by ceric oxidation, the excess of ceric ions being removed with sodium azide. Table II also shows results obtained when ceric oxidation was followed by solvent extraction. Interference from iron and copper was greatly reduced, and a twenty-fold excess of these elements produced individual errors of 2 per cent. or less. The combined interference of solution *A* was apparently slightly greater, but much less than without the solvent-extraction stage. As the chromium to be determined in these solutions arose from the corrosion of stainless steel, the ratio of iron to chromium was unlikely to exceed 20. It was only necessary to take a 1·0-ml aliquot for the determination of 10 μg of chromium, and hence the copper present was not likely to exceed 0·3 mg. To test the accuracy and precision of the method, forty-four replicate determinations were carried out at 10 to 90-μg levels of chromium in the presence of 11·4 mg of uranium, 0·305 mg

of copper, 0·106 mg of nickel and 0·105 mg of iron. The mean recovery was 100·3 per cent. and the standard deviation was ± 0·8 per cent.

TABLE II

EFFECTS OF INTERFERING ELEMENTS AND OF SOLVENT EXTRACTION

Each solution contained 50 μg of chromium

Colour developed from chromium^{VI} solution without solvent extraction—

Amount of uranium added, mg	0·0	5·0	10·0	20·0	50·0			
Amount of chromium found, μg	50·0	50·0	49·8	50·0	49·8			
Amount of thorium added, mg	0·0	100	200	300	400			
Amount of chromium found, μg	50·0	50·1	50·0	50·2	50·0			
Amount of nickel added, mg	0·0	0·20	0·53	1·06	5·28			
Amount of chromium found, μg	50·0	50·0	49·9	49·8	50·0			
Amount of copper added, mg	0·0	0·193	0·386	0·579	0·772	0·963	2·0	5·0
Amount of chromium found, μg	50·0	46·3	45·9	45·7	45·7	45·4	43·2	42·5
Amount of iron added, mg	0·0	0·255	0·510	0·765	1·02	1·25	2·50	6·25
Amount of chromium found, μg	50·0	47·7	46·5	45·7	45·7	43·5	43·5	44·0
Amount of solution *A* added, ml*	0·0	0·5	1·0	2·0				
Amount of chromium found, μg	50·0	44·0	42·7	40·7				

Colour developed after ceric oxidation and solvent extraction of chromium^{III} solution—

Amount of copper added, mg	0·0	0·2	0·4	0·6	0·8	1·0	1·93	4·8
Amount of chromium found, μg	50·0	49·7	49·7	49·7	49·4	49·2	48·9	47·0
Amount of iron added, mg	0·0	0·255	0·510	0·765	1·02	1·25	2·50	6·25
Amount of chromium found, μg	50·0	49·7	49·8	49·2	49·0	48·2	47·2	46·5
Amount of solution *A* added, ml*	0·0	0·5	1·0	2·0				
Amount of chromium found, μg	50·0	49·5	49·1	49·8				

* Solution *A* contained, per millilitre, 11·4 mg of uranium, 0·305 mg of copper, 0·1056 mg of nickel and 0·1251 mg of iron.

Anions—Oxidations were carried out in the presence of 400 mg of nitrate ion and trace amounts of chloride, perchlorate and fluoride; no interference was observed.

METHOD

REAGENTS—

Ammonium hexanitratocerate, 0·02 N—Dissolve 10·965 g of analytical-reagent grade ammonium ceric nitrate, $(NH_4)_2Ce(NO_3)_6$, in water. Make the solution *N* with respect to sulphuric acid when diluted to 1 litre.

Sulphuric acid, 4 N.

Hydrochloric acid, 4 M.

Hexone saturated with M *hydrochloric acid*—Shake 500 ml of *iso*butyl methyl ketone with 500 ml of *M* hydrochloric acid, and allow the layers to separate. Run off the aqueous layer and pass the solvent layer through a Whatman No. 1 filter-paper into a clean dry bottle.

Diphenylcarbazide solution, 1 per cent. w/v—Dissolve 0·5 g of diphenylcarbazide in acetone and dilute to 50·0 ml with acetone. Prepare this solution freshly each day.

Standard chromium potassium sulphate solution, 1·00 mg per ml—Dissolve 4·8031 g of analytical-reagent grade chromium potassium sulphate, $CrK(SO_4)_2.12H_2O$, in water, add a few millilitres of 4 *N* sulphuric acid and dilute to 1 litre. For calibration purposes, dilute 10·0 ml of this solution to 1 litre.

PROCEDURE—

Place an aliquot containing 10 to 90 μg of chromium in a 40-ml centrifuge tube. Neutralise any excess of free acid with ammonium hydroxide, and then make slightly acid with sulphuric acid. If ferrous iron is known to be present, oxidise it to the ferric state with 0·02 *N* ammonium hexanitratocerate. Add 2·0 ml of 4 *N* sulphuric acid and 2·0 ml of 0·02 *N* ammonium hexanitratocerate, dilute to about 15 ml, and immerse in boiling water for 25 minutes. Remove, and cool to $\leqslant 10°$ C. Add 8·0 ml of 4 *M* hydrochloric acid while the solution is cooling. Transfer to a 100-ml calibrated separating funnel, and dilute to 32 ml with water. Add 20·0 ml of hexone saturated with *M* hydrochloric acid. Shake for 1 minute, allow the layers to separate, and then run off and discard the aqueous layer. Add 20·0 ml of water to the separating funnel, and shake for 1 minute. When the layers have separated, run the

aqueous layer into a 100-ml calibrated flask containing 5·0 ml of 4 *N* sulphuric acid. Repeat the washing with a further 20·0 ml of water, and add it to the previous washings. Dilute to about 90 ml, and add 2·0 ml of 1 per cent. diphenylcarbazide solution. Dilute to the mark and set aside for 5 minutes. Measure the optical density against water in 2-cm cells with a Spekker absorptiometer, Ilford No. 605 filters and a mercury-vapour lamp being used. Prepare a blank solution in the same manner and measure its optical density against water.

Prepare a calibration graph from aliquots of chromium potassium sulphate solution in the range 10 to 90 μg of chromium, to which interfering elements in the concentrations expected in the samples have been added.

Conclusions

Compared with other published methods, the proposed method has been found to be rapid and reliable. The interference from iron is not likely to exceed 2 per cent. in the worst conditions envisaged. The method has been extended to solutions obtained from the erosion and corrosion of stainless steel by thoria slurries.

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The Determination of Nickel by a Solvent-extraction Method

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A method is described for the rapid determination of nickel in solutions containing uranium, thorium, copper, iron and chromium. The aqueous insoluble 4-methyl*cyclo*hexane-1:2-dionedioxime complex of nickel is extracted with toluene, and the optical density of this phase is measured with a Spekker absorptiometer, a Hilger H556 filter being used. Interference by copper is suppressed with thioglycollic acid, and tartaric acid is used to prevent formation of iron thioglycollate. Tartrate also prevents the hydrolysis of thorium.

A rapid method for determining small amounts of nickel in solutions containing uranium, thorium, copper, iron and chromium was required. Methods in which ion-exchange techniques are used have been developed[1] for radioactive solutions containing these elements, but the procedures are extremely exacting and time-consuming.

Many analogues of dimethylglyoxime have been suggested for colorimetric and gravimetric determinations of nickel. The nickel complexes can be extracted with organic solvents, *e.g.*, nickel has been determined absorptiometrically after extraction of its α-furildioxime complex with chloroform.[2] This method was tried in our laboratories, but the results were not reproducible, and further, the range of 0 to 20 μg was too limited for our requirements. Banks and Hooker[3] described a reagent, 4-methyl*cyclo*hexane-1:2-dionedioxime (4-methylnioxime), for the gravimetric determination of nickel in the pH range 3 to 7. They studied the interference of some twenty-nine elements, and their results suggested that the reagent would be suitable for our purpose.

Experimental

Approximately 50 μg of nickel were precipitated with a 0·1 per cent. aqueous solution of 4-methylnioxime from a solution buffered at pH 5 to 5·5 with ammonium acetate. The red precipitate first appeared as a colloid, which rapidly coagulated under these conditions.

Attempts were made to extract the precipitate with a variety of organic solvents; the results are shown in Table I. Toluene was found to be the best solvent, extraction being rapid and complete in one stage. The organic phase was yellow, and, when measured with a Unicam spectrophotometer, showed a broad absorption band with a maximum at 340 mμ. (The molar extinction coefficient at 365 mμ is 3340.) The colour was stable for at least 2 hours, and Beer's law was obeyed over a concentration range of 5 to 200 μg of nickel per 25 ml of toluene.

TABLE I

SOLUBILITY OF NICKEL - 4-METHYLNIOXIME COMPLEX IN VARIOUS ORGANIC SOLVENTS

Extractions were carried out from solutions containing 100 μg of nickel and 1·0 ml of 10 per cent. w/v sodium acetate solution

Solvent	Solubility	Colour of solvent phase
*iso*Butyl methyl ketone (industrial) ..	Slightly soluble	Faint yellow
Chloroform	Slightly soluble	Pale yellow
sec.-Butyl alcohol	Slightly soluble	Red
Carbon tetrachloride	Slightly soluble	Pale yellow
*iso*Amyl alcohol	Slightly soluble	Red
Di-*n*-butyl ether	Insoluble	—
*iso*Butyl methyl ketone (pure)	Insoluble	—
*cyclo*Hexane	Insoluble	—
n-Hexane	Insoluble	—
Ethyl acetate	Insoluble	—
Benzene	Readily soluble	Yellow
Toluene	Highly soluble	Yellow

EFFECT OF INTERFERING IONS—

Cations—For each of the ions expected to accompany nickel in sample solutions, the following procedure was used to determine individual and collective interference. A solution containing a suitable concentration of the interfering element or elements was buffered at pH 4 with ammonium acetate. One millilitre of 0·1 per cent. 4-methylnioxime solution was added and the solution was extracted with toluene. Precipitation was not apparent in any solution. Tartaric acid was added to the solution containing thorium to prevent hydrolysis. The absorption spectra of the toluene phases were examined; those derived from solutions containing uranium, thorium, iron and chromium showed no absorption in the region of 365 mμ, the wavelength transmitted by a Hilger H556 filter. In this region, however, copper caused an absorption band similar to that of nickel. Various methods of masking were tried, *e.g.*, ethylenediaminetetra-acetic acid, ammonia, citrate, tartrate, cyanide and ammonium thiocyanate after reduction of copper to the cuprous form with sulphur dioxide, but none was satisfactory. Pellowe and Hardy[4] described the use of thioglycollic acid for masking copper in the analysis of aluminium. It was found that 1·0 ml of 10 per cent. thioglycollic acid solution prevented formation of the copper - 4-methylnioxime complex. It was then necessary to add tartaric acid and to use sodium hydroxide instead of ammonium hydroxide for neutralising free acid to prevent interference from iron thioglycollate. In the presence of tartaric acid the optimum pH was 5 to 5·5.

Anions—Extractions were carried out in solutions containing a hundred-fold excess of sulphate, chloride and nitrate without interference. In the presence of citrate, precipitation was retarded and recoveries were low.

METHOD

REAGENTS—

Sodium hydroxide, 2 N.

Thioglycollic acid solution, 10 *per cent. v/v*—Dissolve 10·0 ml of analytical-reagent grade thioglycollic acid in water and dilute to 100 ml. The solution is stable for about 1 month.

Sodium acetate solution, 10 *per cent. w/v.*

Tartaric acid solution, 20 *per cent. w/v.*

4-Methylnioxime solution, 0·1 *per cent. w/v*—Dissolve 0·1 g of 4-methyl*cyclo*hexane-1 : 2-dionedioxime in water and dilute to 100 ml. The solution is stable indefinitely.

Standard nickel solution—Dissolve approximately 24 g of nickel sulphate, $NiSO_4.7H_2O$, in water and dilute to 1 litre. Standardise the solution gravimetrically.

PROCEDURE IN PRESENCE OF THORIUM, IRON AND CHROMIUM—

Place an aliquot containing 5 to 100 μg of nickel in a 50-ml beaker, and add sufficient 20 per cent. w/v tartaric acid solution to prevent hydrolysis of thorium. Add 1·0 ml of 10 per cent. w/v sodium acetate solution, and adjust the pH to between 5 and 5·5 with 2 *N* sodium hydroxide. Transfer the solution to a 100-ml separating funnel, add 1·0 ml of 0·1 per cent. 4-methylnioxime solution, and dilute to 30 ml with distilled water. Add exactly 25 ml of sulphur-free toluene, and shake for 2 minutes. Allow the layers to separate and run off the aqueous layer. Pass the solvent layer through a Whatman No. 1 filter-paper, to remove the last traces of water, into a clean dry 2-cm absorptiometer cell, and cover the cell to prevent evaporation. Measure the optical density with a Spekker absorptiometer fitted with H556

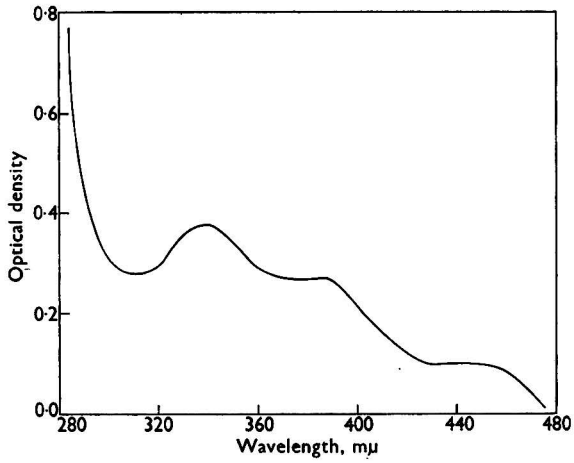

Fig. 1. Absorption spectrum of the nickel - 4-methylnioxime complex in toluene: the complex was prepared from 105 μg of nickel and 1·0 ml of 0·1 per cent. 4-methylnioxime solution in 25 ml of toluene, and the optical densities were measured in a 1-cm cell

TABLE II

EFFECT OF OTHER ELEMENTS ON THE DETERMINATION OF NICKEL

All solutions contained 1·0 ml of 10 per cent. w/v sodium acetate solution, 1·0 ml of 20 per cent. w/v tartaric acid solution and 1·0 ml of 10 per cent. v/v thioglycollic acid solution

Solution	Uranium present, mg	Thorium present, mg	Copper present, mg	Iron present, mg	Chromium present, mg	Nickel added, mg	Nickel found, mg
1	11·0	—	—	—	—	0·0	0·0
2*	—	46·0	—	—	—	0·0	<0·001
3	—	—	0·963	—	—	0·0	0·0
4	—	—	—	1·02	—	0·0	<0·001
5	—	—	—	—	0·236	0·0	<0·001
6	—	—	—	—	—	0·132	0·132
7	—	—	—	—	—	0·0528	0·053
8	11·0	—	0·482	0·102	0·250	0·132	0·132
9	11·0	—	0·482	0·255	0·250	0·132	0·131
10	11·0	—	0·482	0·510	0·250	0·132	0·130
11	11·0	—	0·241	0·102	0·250	0·132	0·129
12	11·0	—	0·241	0·255	0·250	0·132	0·130
13	11·0	—	0·241	0·510	0·250	0·132	0·130
14	11·0	—	—	—	0·250	0·132	0·130
15	11·0	—	0·241	0·102	0·025	0·0528	0·053
16*	—	37·5	—	1·38	0·221	0·132	0·132
17†	5·38	104·5	0·150	0·051	0·047	0·0504	0·050
18†	5·38	104·5	0·150	0·051	0·047	0·1032	0·1035
19†	5·38	104·5	0·150	0·051	0·047	0·156	0·155

* Solution contained no thioglycollic acid.
† Solution contained 2 ml of 20 per cent. w/v tartaric acid solution.

filters and a mercury-vapour lamp. Use a blank solution, prepared in a similar manner, in the comparison cell.

PROCEDURE IN PRESENCE OF URANIUM, COPPER, IRON AND CHROMIUM—

Place an aliquot containing 5 to 200 μg of nickel in a 50-ml beaker, and add 1·0 ml of 20 per cent. w/v tartaric acid solution. Add 1·0 ml of 10 per cent. v/v thioglycollic acid solution and 1·0 ml of 10 per cent. w/v sodium acetate solution. Adjust the pH to between 5 and 5·5 against a pH meter with 2 *N* sodium hydroxide, and continue as described under "Procedure in Presence of Thorium, Iron and Chromium."

PREPARATION OF CALIBRATION GRAPH—

Take aliquots of standard nickel solution to cover the range 5 to 200 μg of nickel and use the procedures described.

RESULTS AND CONCLUSIONS

Fig. 1 shows the absorption spectrum of the nickel - 4-methylnioxime complex. Table II shows the effect of cations on the nickel determination. Eighteen replicate determinations were carried out at 50, 100 and 150-μg levels of nickel in the presence of 6 mg of uranium, 0·15 mg of copper, 104 mg of thorium, 0·05 mg of iron and 0·05 mg of chromium; the mean recovery was 99·8 per cent. and the standard deviation was $\pm$1·2 per cent.

The proposed method is rapid, simple and accurate; it has been used constantly in our laboratories for the last 6 months.

We thank Mr. R. Todd and Mr. W. H. Hardwick for helpful discussions during this work.

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The Determination of Magnesium in Solution by Direct Photometry

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The spectrochemical determination of magnesium in solution by the porous-cup - spark method has been greatly facilitated by the direct photometer described. The magnesium line at 2802 A is used with the strontium line at 4077 A as internal standard. Solutions containing from 0·3 to 24 p.p.m. of magnesium are analysed directly with a coefficient of variation of about $\pm$2·0 per cent. at a rate of forty determinations per hour. Interferences are found to be negligible for most types of agricultural samples, such as extracts of soils and plant materials.

IN agricultural laboratories, many thousands of samples have to be analysed each year for potassium, sodium, calcium and magnesium. Of these elements, the first three can be determined conveniently by flame photometry, especially when a multi-channel instrument is available.[1] The determination of magnesium in this manner is unsatisfactory. In the first place, magnesium is not very sensitive in the flame and solutions generally have to be concentrated before adequate sensitivity is achieved. Secondly, the most sensitive flame line at 2851 A lies in an (OH)-band system, and, at the low concentrations required, some form of background correction is necessary.

For the past few years, a spectrographic technique in which the porous-cup - spark method of excitation[2] is used has been employed at the Macaulay Institute for determining magnesium in soil and plant extracts. The sensitivity is such that magnesium, in the range 0·3 to 24 p.p.m. in solution, can be determined without further concentration in the acetic

acid soil extract used for the flame-photometric determination of readily soluble potassium, sodium and calcium in soils. This spectrographic method proved to be so satisfactory that a direct-reading attachment for a Hilger small-quartz spectrograph has been constructed specifically for determining magnesium by the porous-cup method.

Description of Apparatus

Direct-reading attachment—

The plate-holder mounting of an E484 Hilger small-quartz spectrograph has been removed, and, in its place, the direct-reading attachment is fitted to the spectrograph casting. Two optical channels are provided, one for the magnesium line at 2802 A and the other for a strontium internal-standard line at 4077 A.

Fig. 1 shows schematic diagrams of the attachment and Fig. 2 shows a view of the interior. A steel backplate, A, slotted for the light beam, is bolted to the spectrograph casting. This plate bears guide rails, B, which carry two slides, C. These slides provide a coarse adjustment parallel to the focal plane and can be clamped by the guide rails. The magnesium slide is slotted to pass the magnesium line and carries a small 90° quartz prism, D, which reflects the magnesium line to an exit slit, as shown in Fig. 1 (*c*). The slides carry shelves, E, hung from brackets, F, by beryllium - copper springs, G. On these shelves are mounted the slit units and holders for the photomultiplier tubes. An independent movement of each shelf along the focal plane is provided by micrometer screws, H and J, which act against the appropriate double-spring assembly.

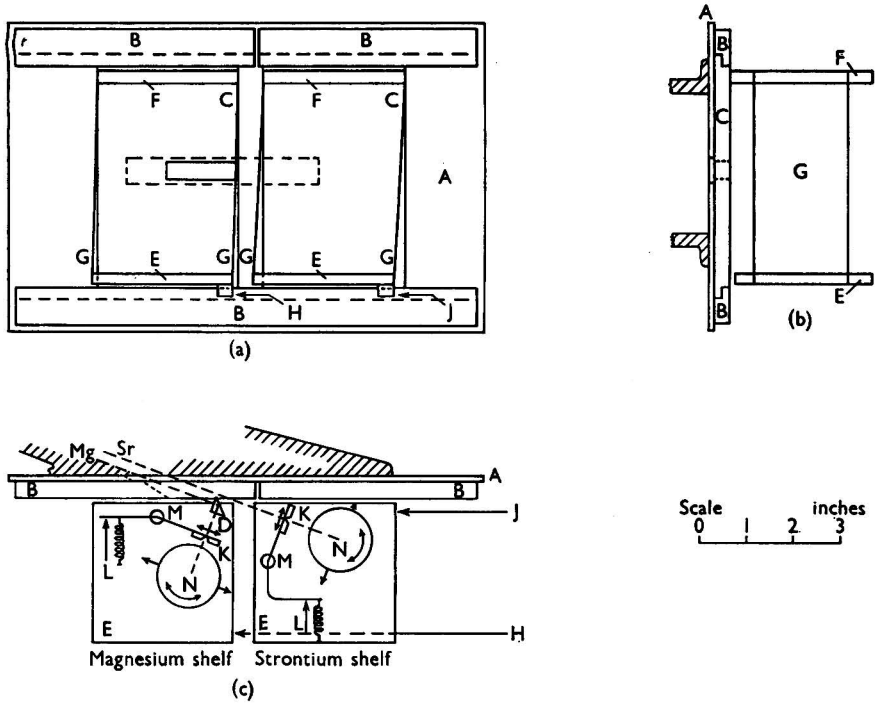

Fig. 1. Schematic diagram of the direct-reading attachment for a Hilger small-quartz spectrograph: A, steel backplate; B, guide rails; C, slides; D, quartz prism; E, shelves; F, shelf brackets; G, beryllium - copper springs; H and J, micrometer screws; K, exit slits; L, slit-focusing screws; M, pivots; N, photomultiplier tubes

Fig. 1(*a*). Elevation

Fig. 1(*b*). Side view

Fig. 1(*c*). Plan

The slits, K, Fig. 1 (*c*), are supported on pivots, M, mounted on the shelves, E. The slits are fitted to brass discs that can be rotated to align them parallel to the entrance slit. The slits can be moved approximately ± 2 mm along the axis of the emergent light beams

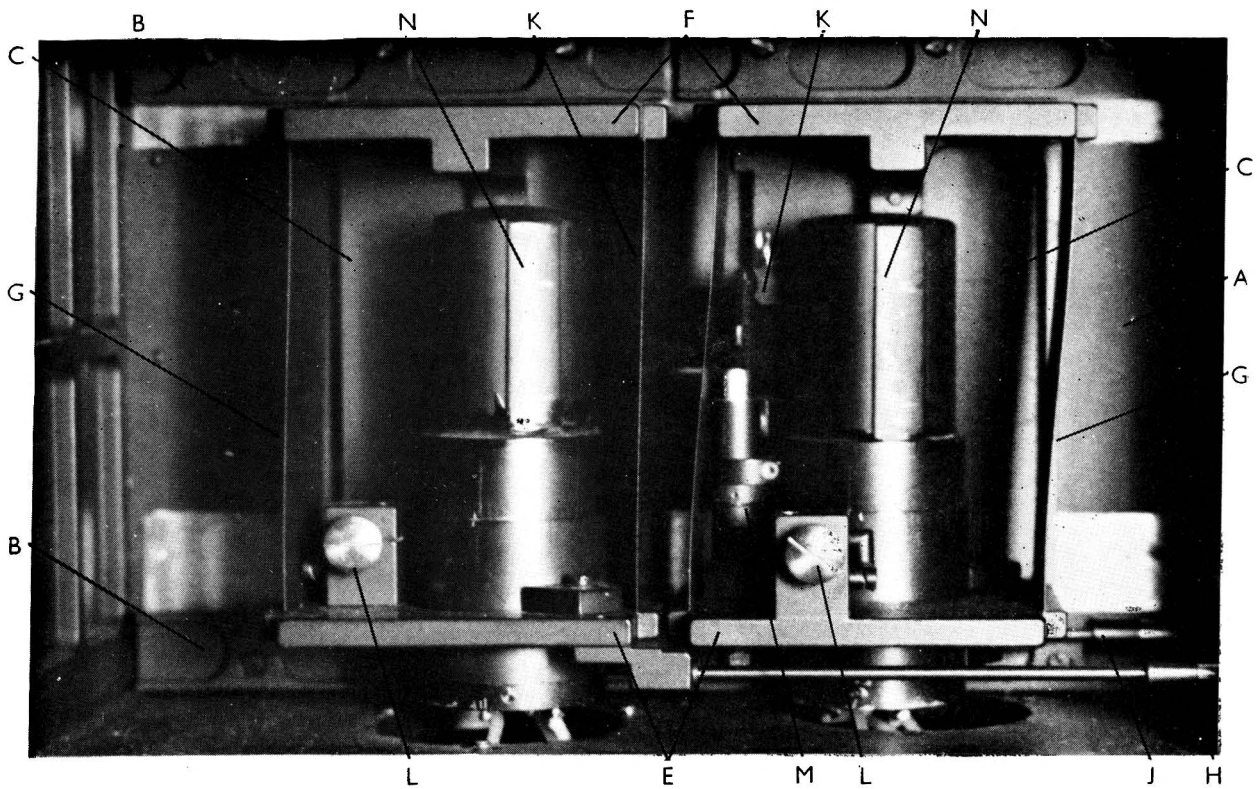

Fig. 2. View of the interior of the attachment: lettered as for Fig. 1

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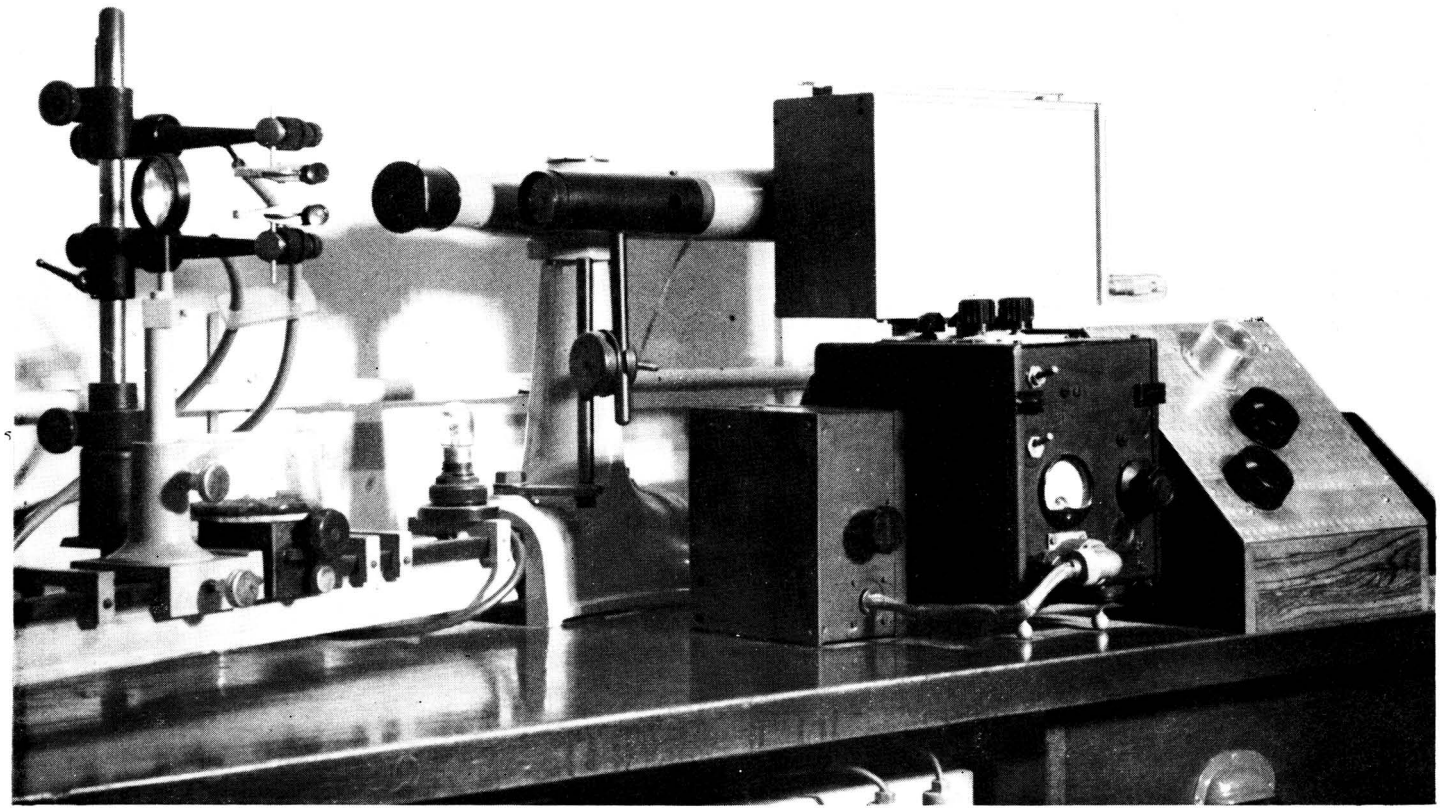

Fig. 4. Equipment for the direct photometric determination of magnesium, showing adaptor fitted to spectrograph: left to right on bench; galvanometer shunt unit, integrating unit with switches on top and measuring potentiometer unit. The Cambridge galvanometer is placed behind the potentiometer, readily visible to the operator; the power pack is situated under the bench

by means of screws, L, which act through pivots M, and by a similar amount across the axis of the beam. On account of the curvature of the spectral lines, the width of each exit slit was made greater than that of the entrance slit. A 3-mm × 0·02-mm entrance slit is used, with fixed-width exit slits of 10 mm × 0·05 mm for magnesium and 10 mm × 0·1 mm for strontium. A piece of suitably exposed and developed photographic plate, which serves as a neutral filter, is mounted behind the strontium exit slit to reduce the light intensity on the strontium photomultiplier tube.

To facilitate the initial setting up, a piece of photographic film was held against the face of the slit and the image of the line was recorded on it. Without being moved, the film was then exposed to light through the slit from the back. The film thus recorded the position of the spectral line image relative to the slit. A convenient accessory for this operation is an iron film-holder held against the face of the slit by a button magnet (Eclipse type A) placed against the back of the slit. A miniature lamp mounted inside the magnet serves to record the slit image. For the final more accurate setting, provision is made in the electronic circuitry for profiling either line by using the instantaneous voltage developed in a resistor by the photomultiplier current.

After removal of the bases, each photomultiplier tube, N, with its resistance chain was fitted into a 40-mm diameter brass tube so as to project about 45 mm above the rim of the tube. These brass tubes were then filled with Di-jell 171 wax (obtained from Astor Boisselier and Lawrence Ltd.), and opaque plastic covers, with windows opposite the photocathodes, were fitted over the photomultiplier tubes. The RCA 1P28 photomultiplier tube used for magnesium had, at 950 volts, a dark current of 5×10^{-11} ampere, compared with 8×10^{-9} ampere before removal of its base.

The brass tube carrying the photomultiplier and resistance chain is a sliding fit in a second brass tube, which is mounted on shelf E. The photomultiplier can therefore be rotated and moved vertically into its correct position before it is clamped. A cross-movement of the whole photomultiplier mount of about ± 2 mm is provided. The direct-reading attachment is light-proof, and has slides at the top and back. Parts inside the box are blackened, and the entire attachment is electrically earthed.

Integrating photometric equipment—

The instrument has an integrating circuit in which the photomultiplier output current charges a condenser. The voltage developed in the condenser is a measure of the total light energy received and is measured by a null-reading electrometer - bridge circuit. The method used is basically that of Naish and Ramsden.[3]

The circuit is shown in Fig. 3. A 1P28 photomultiplier tube, V_{11}, is used for the magnesium line and a 931A photomultiplier tube, V_{12}, for the internal-standard strontium line. V_{11} is operated at about 950 volts, but V_{12} has its voltage reduced to about 700 volts by resistor R_{16}. Both voltages are supplied from a stabilised power pack, as shown in Fig. 3 (a). In addition, the 50-cycle mains voltage supply to the laboratory is controlled by a Ferranti voltage regulator, with a voltage stability of $\pm 0{\cdot}5$ per cent. The complete apparatus is shown in Fig. 4.

When a determination is made, the integrating condenser for magnesium, C_4, is connected in by S_5 and that for strontium, C_6 or C_7, is selected by S_6. With the measuring potentiometer, R_{17}, at zero and switches S_3 and S_4 at position 1, the integration is started by setting S_3 to position 2. The photomultiplier currents then charge their respective condensers until, at the end of the exposure, S_3 is switched to position 3 and the two condensers are isolated preparatory to measuring their voltages. To measure the voltage of the magnesium condenser, S_4 is switched to position 2 and the measuring potentiometer, R_{17}, is turned until an equal and opposite voltage is applied to the electrometer grid to balance the condenser voltage, as shown by a zero reading on galvanometer M_3. To measure the voltage of the internal-standard (strontium) condenser, R_{17} is returned to zero, S_4 is switched to position 3 and the required angular rotation of R_{17} is read as before. The cycle of operations is completed and the instrument is re-set for further determinations by returning R_{17} to zero and S_3 and S_4 to position 1.

R_{17} is a linear-law potentiometer, and thus the ratio of the magnesium and strontium angular rotations is proportional to the ratio of the magnesium and strontium condenser voltages and hence to the ratio of the relative intensities of the magnesium and strontium

spectral lines. A 5-inch diameter 360° plastic protractor, illuminated from below, is used as the scale for R_{17}.

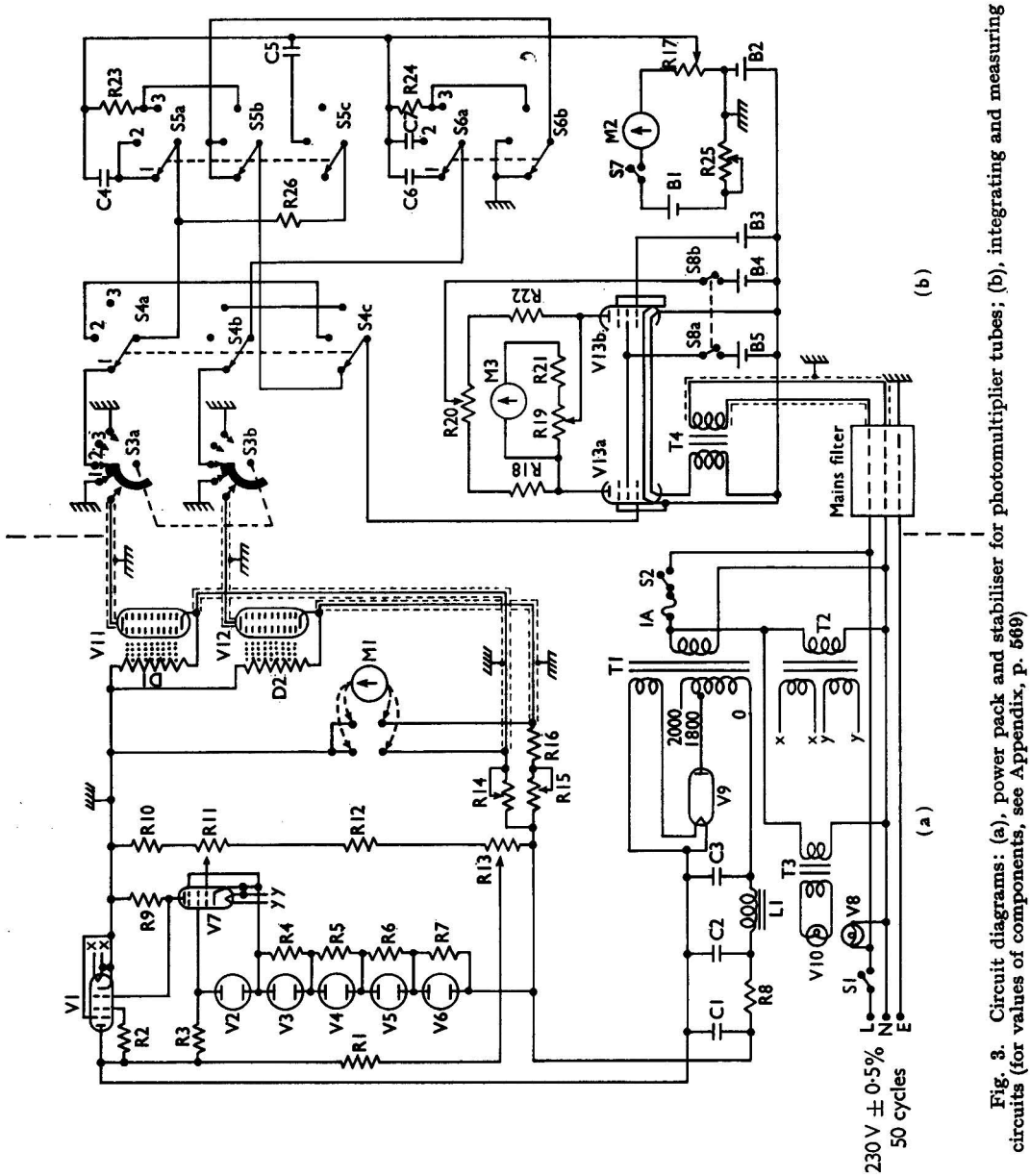

Fig. 3. Circuit diagrams: (a), power pack and stabiliser for photomultiplier tubes; (b), integrating and measuring circuits (for values of components, see Appendix, p. 569)

Either line can be profiled by using the instantaneous voltage developed by the photomultiplier current in a resistor (R_{23} or R_{24}). To profile the magnesium line, for example, S_5 is set at position 3, S_6 at position 1 or 2, S_4 at position 1 and S_3 at position 2.

Excitation and operating conditions

The porous-cup electrodes used for the determination of magnesium are made from 5·5-mm diameter carbon rods, obtained from C. H. Champion & Co. Ltd. (less-pure grade). The cups are approximately 16 mm long and have a bore of 3·2 mm ($\frac{1}{8}$ inch), a drill with an included angle of 135° being used. The base thickness is 0·60 ± 0·01 mm and no pre-heating or pre-sparking of the empty electrode is necessary. The counter-electrode has a sharp

point of 70° included angle. The spark gap is 2 mm and is not adjusted during the exposure.

The source is an uncontrolled Hilger-type spark of 15,000 volts with 0·02-mH inductance, 0·001-μF capacitance and no added resistance. With these parameters, a relatively weak undamped spark is produced.

Strontium has proved to be a suitable internal standard and is present in only small amounts in the materials being examined, so that a constant standard addition can be made, provided it is large enough.

The magnesium to strontium ratio for a solution is determined by filling the porous cup with solution and sparking for 56 seconds. The direct reader is set to the integrating position, with the slit open, immediately before the spark is made, and sparking is stopped by a time switch after the discharge has continued for 56 seconds. During this period, about 0·11 ml of solution is consumed. All solutions to be analysed contain 500 p.p.m. of strontium and 2·0 to 2·25 per cent. of acetic acid. The voltage ratio is calculated from the angular rotations of R_{17}, as described previously. The voltage of the magnesium condenser, which can be measured by R_{17}, is limited by B_1 (see Fig. 3) to about 8 volts. If the solution tested gives too high a voltage with the 0·05-μF magnesium condenser, C_4, the series combination of the nominal 0·1-μF condenser, C_5, and resistor R_{26} is switched in in parallel with C_4, the charge of which is then distributed over a total capacity of about 0·15 μF. The voltage is thus lowered to a readable value without the necessity for a second exposure. Resistor R_{26} is included to limit excessive current surges at this switching action. Should even higher magnesium contents have to be determined, provision could be made to incorporate further condensers in parallel with C_4 and C_5.

The porous cup is placed 20 cm from the entrance slit with no condensing lens. With the nominal 0·05-μF condenser used for the magnesium line at 2802 A and the 1P28 photomultiplier tube operated at about 950 volts, 6 p.p.m. of magnesium produce a condenser voltage of about 5·6 volts, 0·3 p.p.m. of magnesium about 0·72 volt and a blank solution (containing only strontium and acetic acid) about 0·24 volt. The dark current produces a condenser voltage of about 0·05 volt.

A 0·1-μF condenser is used for the strontium line at 4077 A. A reduced voltage of about 700 volts to the 931A photomultiplier tube and a neutral filter behind the exit slit are required to lower the condenser voltage to a readable value. Other available strontium lines are not suitable, those at 4161 and 4215 A are in a band system, that at 4305 A is interfered with by calcium and that at 4607 A, which is almost as strong as the line at 4077 A, is an arc line. It is undesirable to reduce the added amount of strontium to less than 500 p.p.m. because a few parts per million may be present in the original solution.

EFFECT OF VARIATION IN ELECTRODE PARAMETERS—

Base thickness of the porous cup—Table I shows the effect of change in the base thickness of the porous cup on the relative intensities and intensity ratios of the magnesium and strontium lines. Each result is an average of seven replicate determinations. There is apparently a depression of the observed magnesium to strontium ratio with increase in base thickness, the relative intensity of strontium increasing more rapidly than that of magnesium. Such changes in base thickness as occur during preparation of the cups should introduce only very small errors.

TABLE I

EFFECT OF CHANGE IN BASE THICKNESS OF THE POROUS CUP

Each determination was carried out in presence of 3 p.p.m. of magnesium

Base thickness, mm	Relative intensity of magnesium	Relative intensity of strontium	Intensity ratio (Mg to Sr)	Error in magnesium content, %
0·40	125·0	148·8	0·839	+5·7
0·60	129·3	161·1	0·802	0·0
0·80	131·9	168·8	0·782	−2·4

Counter-electrode shape—Table II shows the effect of different shapes of counter-electrode. Each result is an average of six replicate determinations and the apparent magnesium contents were read from a standard curve prepared by using counter-electrodes with 70° points. It can be seen that, when rods with flat tops were used as counter-electrodes, both the relative

intensities and the intensity ratio increased with the diameter, the relative intensity of magnesium increasing more rapidly than that of strontium. When pointed rods were used, both the relative intensities and the intensity ratio increased with the included angle of the point, but much more slowly than with increase in rod diameter. Little change in the intensity ratio is found for points with included angles between 70° and 90°.

TABLE II

EFFECT OF COUNTER-ELECTRODE SHAPE

Each determination was carried out in presence of 1·2 p.p.m. of magnesium

Rod diameter, mm	Included angle	Relative intensity of magnesium	Relative intensity of strontium	Intensity ratio (Mg to Sr)	Error in magnesium content, %
Flat-topped counter-electrode—					
2·0	—	43·9	113·2	0·388	+8
2·5	—	58·8	136·3	0·431	+23
3·0	—	71·7	152·5	0·468	+37
4·0	—	96·7	174·3	0·555	+73
5·5	—	158·9	237·3	0·669	+110
Pointed counter-electrode—					
—	50°	43·1	129·2	0·334	−8·4
—	60°	44·9	133·6	0·337	−6·7
—	70°	46·7	130·3	0·358	0·0
—	80°	52·0	147·3	0·353	−1·8
—	90°	53·9	148·3	0·364	+2·7
—	110°	62·7	156·1	0·395	+14·1
—	125°	74·3	167·1	0·443	+30·8

Length of spark gap—The effect of change in the length of spark gap on the intensity ratio is shown in Table III. Increase in the gap length produces only a slight increase in intensity ratio and apparent magnesium content, although the individual relative intensities increase considerably. In practice, an optical projection system is used to position the electrodes and the gap is set to within ±0·05 mm of 2·0 mm. No error should result from such slight changes in the gap length.

TABLE III

EFFECT OF THE LENGTH OF SPARK GAP

Each determination was carried out in presence of 1·2 p.p.m. of magnesium

Gap length, mm	Relative intensity of magnesium	Relative intensity of strontium	Intensity ratio (Mg to Sr)	Error in magnesium content, %
1·5	42·1	130·5	0·323	−0·5
2·0	53·1	163·5	0·325	0·0
2·5	58·7	174·5	0·336	+4·0
3·0	72·1	209·9	0·343	+6·9

TABLE IV

EFFECT OF VARIATION IN POSITION OF ELECTRODES ACROSS THE OPTICAL AXIS

Each determination was carried out in presence of 1·8 p.p.m. of magnesium

Distance moved across optical axis,* mm	Relative intensity of magnesium	Relative intensity of strontium	Intensity ratio (Mg to Sr)	Error in magnesium content, %
+2·8	55·1	124·0	0·444	+7·7
+2·1	52·2	125·6	0·416	−0·4
+1·4	56·6	133·3	0·423	+1·4
+0·7	59·4	142·7	0·416	−0·4
0	58·5	139·7	0·418	0·0
−0·7	57·6	128·9	0·446	+8·4
−1·4	59·2	130·8	0·453	+10·5
−2·1	57·7	119·1	0·485	+20·3
−2·8	61·0	111·3	0·547	+40·4

* Distance measured from an arbitrary zero position.

Position of electrodes on optical axis—Instantaneous current readings, by means of the profiling circuits, were taken while the discharge was moved horizontally across the optical axis. A constant current was obtained for magnesium over about ±3 mm and for strontium over about ±1·5 mm. Similarly, on the vertical axis, constant currents were found for magnesium over ±8 mm and for strontium over ±5 mm. The vertical position of the electrodes does not appear to be critical.

The effect of moving the spark across the axis is shown in Table IV, an arbitrary zero position being taken within the constant current region. It can be seen that, over a range of 2·1 mm (from +2·1 mm to the zero position) the magnesium to strontium ratio is constant. With the working position set at +1·0 mm, small changes in the horizontal position of the electrodes should not affect the results.

Discharge conditions—Several sparking procedures that gave good reproducibility are compared in Table V. The results are from twenty replicate determinations by each procedure. It can be seen that procedure C is better than A or B and is also the simplest. In procedures A, B and C the electrodes were taken consecutively from storage racks of two hundred cups and points, as would be done in practice. Procedure D is the same as C except that the electrodes were taken at random from a stock of six hundred cups and points. Procedure C is now used with an expected coefficient of variation of ±1·86 per cent. for a single determination.

TABLE V

STATISTICAL ANALYSIS OF DETERMINATION OF 1·8 p.p.m. OF MAGNESIUM BY DIFFERENT PROCEDURES

In all instances the exposure was 56 seconds and a counter-electrode with a 70° sharp point was used. Each result is the average of twenty replicate determinations, and was obtained from a standard curve prepared by using procedure A

Procedure	Amount of solution used	Time of pre-sparking, seconds	Mean amount of magnesium found, p.p.m.	Standard deviation, p.p.m.	Coefficient of variation, %	Maximum negative error, %	Maximum positive error, %
A*	0·11 ml	15	1·793	0·0496	±2·76	4·8	6·1
B†	Full cup	15	1·942	0·0549	±2·85	4·8	7·5
C‡	Full cup	Nil	1·648	0·0306	±1·86	3·5	2·9
D§	Full cup	Nil	1·660	0·0401	±2·41	3·5	4·6

* Spark gap was re-set to 2·0 mm after pre-sparking with cup empty.
† Spark gap was not re-set after pre-sparking with cup empty.
‡ Spark gap was set to 2·0 mm and not altered during exposure.
§ As for procedure C, but cups and counter-electrodes were selected at random from stock of 600 of each.

EFFECT OF OTHER VARIABLES—

No change in the magnesium to strontium ratio was observed when the input voltage to the photomultiplier power pack was varied from 240 to 210 volts. Similarly, no change was produced by altering the current from the standard battery, B_1 (see Fig. 3), in the measuring circuit from 458 to 470 mA.

Change in room temperature from 14·5° to 24° C has not caused curve drift, and it would appear that the exit slits are sufficiently wide to take care of any normal temperature change in the surroundings.

Long-term curve drift has occurred at intervals of about 3 months, when it has been necessary to re-set the exit slits by means of micrometer screws H and J (see Figs. 1 and 2). As the exit slits require to be re-set in opposite directions, this is probably the result of the beryllium - copper springs, G (see Figs. 1 and 2), being twisted by the side pressure of the micrometers. The design, in fact, should be modified, so that the micrometers act along the central axes of the springs. To carry out a routine check of exit-slit positions by profiling, freshly prepared hemispherical MG5 aluminium-alloy electrodes are used for magnesium, and, for strontium, a porous cup in which is placed a solution containing 1000 p.p.m. of the element is used.

Short-term curve drift was observed in the early stages of setting up the instrument, when a sphero-cylindrical quartz lens was used to focus the spark on the entrance slit. A slow decrease in intensity ratio was caused by the gradual fogging of this lens, which then

absorbed more of the ultra-violet (magnesium) light than of the visible (strontium) light. No condensing lens is now used between spark and entrance slit.

Effect of extraneous elements—

The amounts of calcium, aluminium, potassium and phosphorus liable to be present in soils and plants and in the extracts used for determining magnesium are shown in Table VI. The effects of the presence of different amounts of these elements on the apparent magnesium content are shown in Table VII. Aluminium, potassium and phosphorus have practically no effect on the apparent magnesium content, most of the errors being within the experimental error of the method. In practice, variation of these elements in soil extracts and plant materials should not produce significant errors. Increase of the calcium present appears to enhance the magnesium content, possibly because the specially purified calcium carbonate used in the preparation of the solutions contained about 50 p.p.m. of magnesium. (The purest commercially available calcium carbonate contained considerably more magnesium.) Extracts of Scottish soils normally contain 50 to 70 p.p.m. of calcium and seldom more than 200 p.p.m. At this level, the effect of variation in the calcium content can be ignored.

Table VI

Amounts of various elements normally present in soil and plant material

	Acetic acid extract of soil		Plant material	
Element	Amount of element present per 100 g of soil, mg	Amount of element present in final solution, p.p.m.	Amount of element present in dry material, %	Amount of element present in final solution, p.p.m.
Calcium	80 to 400	20 to 100	0·05 to 6·0	0·4 to 48
Aluminium ..	80 to 240	20 to 60	0·001 to 1·0	0·008 to 8·0
Potassium ..	2·4 to 80	0·6 to 20	0·15 to 8·0	1·2 to 64
Phosphorus ..	0·4 to 140	0·1 to 35	0·05 to 1·0	0·4 to 8·0

Table VII

Errors in apparent magnesium content in presence of extraneous elements

Calcium		Aluminium		Potassium		Phosphorus and potassium		
Amount of element present, p.p.m.	Error in magnesium content, %	Amount of element present, p.p.m.	Error in magnesium content, %	Amount of element present, p.p.m.	Error in magnesium content, %	Amount of phosphorus present, p.p.m.	Amount of potassium present, p.p.m.	Error in magnesium content, %
Each determination carried out in presence of 0·6 *p.p.m. of magnesium—*								
0	0·0	0	0·0	0	0·0	0	0	0·0
100	0·0	6	+1·0	10	+1·0	10	13	+1·9
500	+5·3	12	−1·0	50	+1·0	50	63	+1·0
1000	+8·5	32	0·0	100	−1·0	100	126	+1·0
—	—	64	−4·1	—	—	—	—	—
Each determination carried out in presence of 3·0 *p.p.m. of magnesium—*								
0	0·0	0	0·0	0	0·0	0	0	0·0
100	+0·2	6	+0·2	10	−0·6	10	13	+0·6
500	+1·8	12	−0·8	50	−0·8	50	63	−0·4
1000	+2·0	32	−0·8	100	−0·8	100	126	+0·2
—	—	64	0·0	—	—	—	—	—

Application to agricultural materials

Acetic acid extracts of soils—

Ten grams of soil are shaken for 2 hours with 400 ml of 2·5 per cent. acetic acid, and the suspension is filtered. Part of the extract is used directly for determining sodium, potassium and calcium by flame photometry. For magnesium, 5 ml of strontium chloride solution (containing 5·0 g of strontium per litre) are diluted to 50 ml with the acetic acid extract. The standard solutions are prepared by diluting 5 ml of strontium chloride solution to 50 ml with stock solutions containing from 0·3 to 24 p.p.m. of magnesium in 2·5 per cent. acetic acid. These solutions are sparked in porous cups as described under "Excitation and Operating Conditions," and the magnesium to strontium intensity ratios are calculated.

Two standard curves are plotted of the magnesium to strontium intensity ratio for the standard solutions against magnesium concentration (in milligrams of magnesium per 100 g of soil). One curve is plotted from 0·3 to 6 p.p.m., the 0·05-μF condenser being used, and another from 6 to 24 p.p.m., the 0·05-μF condenser again being used for the integration, but with the 0·1-μF condenser connected in parallel before measurement of the voltage ratio. Samples with magnesium contents above 24 p.p.m. are diluted with a solution containing 500 p.p.m. of strontium in 2·25 per cent. acetic acid.

AMMONIUM ACETATE EXTRACTS OF SOILS—

Twenty grams of soil are mixed with 100 ml of a *N* solution of neutral ammonium acetate, the suspension is set aside overnight, filtered, and then leached with ammonium acetate solution to a volume of 1 litre.

Five millilitres of strontium chloride solution and 1 ml of glacial acetic acid are diluted to 50 ml with the extract. Acetic acid is necessary to ensure percolation through the porous base of the cup. Standard solutions containing from 0·3 to 24 p.p.m. of magnesium and 500 p.p.m. of strontium are prepared in a base solution of *N* ammonium acetate and 2 per cent. acetic acid. Standard curves are plotted as before for the ranges 0·3 to 6 p.p.m. and 6 to 24 p.p.m. of magnesium.

PLANT MATERIAL—

Ten grams of dry plant material are ashed at 450° C overnight and the ash is twice evaporated to dryness with 2·5 ml of concentrated hydrochloric acid to precipitate silica. The residue is extracted with 25 ml of dilute hydrochloric acid (1 + 4 v/v), filtered, and diluted to 500 ml with distilled water. An aliquot of this solution, generally 2 ml, is placed by pipette in a 50-ml calibrated flask, 5 ml of strontium chloride solution are added, and the solution is diluted to the mark with 2·5 per cent. acetic acid. Standard curves are plotted as before, standard solutions in acetic acid incorporating potassium dihydrogen phosphate, potassium sulphate, calcium carbonate and sodium chloride in proportions corresponding to an average plant ash being used.

Twenty samples of turnips were analysed in duplicate by the proposed method and by a colorimetric procedure with Titan yellow.[4] The mean values for magnesium were, respectively, 0·0687 and 0·0685 per cent. (standard deviations $\pm$0·00168 and $\pm$0·00384 per cent.), but the coefficient of variation was better by the proposed method ($\pm$2·4 per cent.) than by the colorimetric procedure ($\pm$5·6 per cent.). From other statistical comparisons, it would appear, as might be expected, that with the proposed method the coefficient of variation is constant at both high and low magnesium contents, although the standard deviation is constant for the colorimetric procedure.

OTHER MATERIALS—

Because of the high sensitivity of the method and the small effect of extraneous elements, magnesium can be determined in solutions derived from practically any material of agricultural interest. At the dilution required for determining magnesium in most limestones, for example, there are no more than 150 to 200 p.p.m. of calcium present in the final solution, an amount that, as shown previously, has little effect on the results. Similarly, with other materials, after the required dilution the effect of extraneous elements is generally negligible. Materials that have been analysed include woods, limestones, sands and minerals.

The instrument has now been in use for over 2 years and has proved to be thoroughly reliable, three to four hundred magnesium determinations per week being carried out. Some forty determinations per hour are possible. The life of the batteries is at least 1 year under these conditions.

APPENDIX

LIST OF COMPONENTS USED IN THE CONSTRUCTION OF THE POWER PACK AND STABILISER FOR PHOTOMULTIPLIER TUBES AND THE INTEGRATING AND MEASURING CIRCUITS

(Fig. 3)

R_1 = 1-megohm 5-watt resistor (five 200,000-ohm 1-watt carbon resistors in series).
R_2 = 100-ohm ½-watt carbon resistor.
R_3 = 200,000-ohm 5-watt resistor (five 1-megohm 1-watt carbon resistors in parallel).

R_4, R_5, R_6, R_7 = 1·5-megohm ½-watt carbon resistor.
R_8 = 25,000-ohm 15-watt resistor (five 5000-ohm 3-watt wire-wound resistors in series).
R_9 = 15,000-ohm 3-watt wire-wound resistor.
R_{10} = 80,000-ohm 12-watt resistor (four 20,000-ohm 3-watt wire-wound resistors in series).
R_{11} = 35,000-ohm 3-watt wire-wound variable resistor.
R_{12} = 10,000-ohm 5-watt wire-wound resistor.
R_{13} = 20,000-ohm 3-watt wire-wound variable resistor.
R_{14}, R_{15} = 100,000-ohm 3-watt wire-wound variable resistor.
R_{16} = 400,000-ohm 2-watt resistor (four 100,000-ohm ½-watt high-stability carbon resistors in series).
R_{17} = 20,000-ohm ±10 per cent. 10-watt wire-wound linear-law potentiometer (Painton CV25).
R_{18}, R_{21}, R_{22} = 5000-ohm 3-watt wire-wound resistor.
R_{19} = 4000-ohm 3-watt wire-wound variable resistor.
R_{20} = 5000-ohm 3-watt wire-wound variable resistor.
R_{23}, R_{24} = 50-megohm ½-watt high-stability carbon resistor.
R_{25} = 500-ohm 3-watt wire-wound variable resistor.
R_{26} = 1000-ohm ½-watt carbon resistor.
C_1, C_2, C_3 = 0·5-μF condenser, 3·5-kV working.
C_4, C_6 = 0·05-μF TCC Plastapack polystyrene dielectric condenser, 350-volt working.
C_5, C_7 = 0·1-μF TCC Plastapack polystyrene dielectric condenser, 350-volt working.
V_1 = EL38 valve.
V_2, V_3, V_4, V_5, V_6 = CV1070 (7475) valve.
V_7 = EF36 valve.
V_8 = 250-volt 15-watt indicator lamp.
V_9 = CV1111 (R11, V1907) valve.
V_{10} = 6-volt 0·3-ampere indicator lamp.
V_{11} = RCA 1P28 photomultiplier tube.
V_{12} = RCA 931A photomultiplier tube.
V_{13} = 28D7 (Sylvania) valve.
B_1, B_4 = 9-volt grid bias.
B_2 = 4·5-volt section of 9-volt grid bias.
B_3 = 6-volt section of 9-volt grid bias.
B_5 = 15-volt Ever Ready Batrymax B121.
D_1, D_2 = Voltage dividers (ten 100,000-ohm ½-watt high-stability carbon resistors in series).
L_1 = Low-frequency choke.
M_1 = 0–2000-volt electrostatic voltmeter.
M_2 = 0–500-μA moving-coil microammeter.
M_3 = 450-ohm Cambridge spot galvanometer, 180 mm per μA.
S_1, S_2, S_7 = Single-pole ON - OFF switch.
S_3 = 2-section 3-postion shorting switch, with silicone-treated ceramic insulation and non-shorting moving contacts.
S_4, S_5, S_6 = 3-section 3-position switch, with silicone-treated ceramic insulation and non-shorting moving contacts.
S_8 = Double-pole ON - OFF switch.
T_1 = Mains transformer: primary windings, 0–210–230–250 volts; secondary windings, (*a*) 0–1800–2000 volts, 20 mA, (*b*) 4 volts, 2 amperes, 2-kV working.
T_2 = Mains transformer: primary windings, 0–210–230–250 volts; secondary windings, two of 6·3 volts, 1·5 amperes, 2-kV working.
T_3 = Mains transformer: primary windings, 0–230–250 volts; secondary winding, 6·3 volts, 1·5 amperes.
T_4 = Mains transformer: primary windings, 0–200–230–250 volts; secondary winding, 0–30 volts, 2 amperes, multi-tappings, 0–8-volt tapping used.

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The Argentimetric Titration of Halide and Cyanide Ions with Dithizone as Indicator

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Methods are described for the argentimetric titration of halide and cyanide ions with dithizone as indicator. It has been found possible to apply the methods to some practical problems, including the determination of halogens in organic compounds.

THE argentimetric titration of bromide, iodide and cyanide ions with dithizone as extraction indicator has been described by Karabash.[1] His methods have been tried in this laboratory and found to be extremely sensitive. However, since a two-phase system is used, which must be shaken after every addition of titrant, the methods are time-consuming and hardly applicable for general routine use.

In the work described, titrations are carried out either in water - acetone or water - alcohol mixtures. Bromides, iodides and cyanides can be titrated in the presence of considerable amounts of water. Chlorides can only be successfully titrated if the water content of the solution is kept low and a non-aqueous solution of silver nitrate is used as titrant.

The methods have been applied to the determination of halogens in organic compounds, both after digestion by the Carius method and after combustion in oxygen by a modified form of Schöniger's adaptation[2] of Mickl and Pech's method.[3,4] In the application to the Carius method, the precipitate of silver halide from the digestion tube is either dissolved in hot concentrated sulphuric acid and determined by titration with potassium iodide solution, or it is dissolved in concentrated ammonia solution and determined by titration with potassium cyanide solution.

When iodides and bromides in acidified water - acetone solution to which a little dithizone has been added are titrated with silver nitrate solution, the end-point is marked by a change from the green colour of dithizone to the orange-yellow colour of the silver - keto-dithizone complex. During the titration, there appears to be a certain amount of absorption of dithizone by the silver halide precipitate, and, near the end-point, this absorbed dithizone changes to a reddish purple colour, which tends to obscure the final colour change to orange-yellow. This effect can be overcome by adding a very small amount of dithizone initially, and, near the end-point, adding about three to five times the initial amount of dithizone. The red-purple colour is then entirely masked and the end-point is marked by a bright orange-yellow colour.

The titration of chlorides in this manner can only be carried out when the solution to be titrated is a water - acetone mixture containing not more than 3 per cent. of water. The titrant can be silver nitrate in either ethanol or *n*-propyl alcohol. When ethanol is used as solvent, a colour change from green to reddish purple takes place well before the end-point, which is marked by a change in colour from red to yellow. When *n*-propyl alcohol is used as solvent, the colour change is very similar to that produced when iodides or bromides are titrated with aqueous silver nitrate. In view of this, and because of its higher boiling-point, *n*-propyl alcohol is the preferred solvent.

The method devised for determining cyanides is based on the classical Liebig method, in which potassium iodide is added to the alkaline cyanide solution, and the solution is titrated with standard silver nitrate solution. The method depends on the fact that one silver ion combines with two cyanide ions to form a complex ion. When this ratio is exceeded, free silver ions are present and a precipitate of silver iodide is produced. In the proposed method, the titration is carried out in water - alcohol mixture to which a little dithizone has been added. At the end-point, free silver ions are present and there is a sharp change in colour from orange-yellow to a deep red-purple, owing to the formation of the silver - enol-dithizone complex. The sensitivity of the method is about ten times as great as that of the Liebig method and the end-points are extremely sharp when 0·01 *N* silver nitrate is used as titrant. Silver can also be titrated with a standard potassium cyanide solution; this forms the basis of the proposed method for determining chlorine in organic compounds after digestion by the Carius method.

The use of *p*-dimethylaminobenzylidenerhodanine as indicator for the titration of cyanides has been described.[5] Tests in this laboratory indicate that the proposed dithizone method gives greater changes in both colour and intensity than the *p*-dimethylaminobenzylidenerhodanine method, and that it can be applied to initially highly coloured solutions, to which the latter method is inapplicable.

Titration of iodide with silver solution and of silver with iodide solution

Reagents—

Acetone—Commercial grade acetone of low water content is suitable.

Dithizone solution—A 0·01 per cent. solution of dithizone in acetone. This solution should be freshly prepared.

Sulphuric acid, diluted (1 + 1 *v/v*).

Silver nitrate solution—A 0·01 *N* aqueous solution of silver nitrate prepared by diluting an accurately standardised 0·1 *N* solution.

Potassium iodide solution, about 0·01 N—Prepared by diluting a 0·1 *N* solution of potassium iodide that has been standardised gravimetrically.

Procedure—

Titration of iodide with silver nitrate solution—By pipette, put into a 250-ml conical flask an aliquot of the sample solution containing about 0·05 to 0·2 milli-equivalent of iodide ion. Dilute to about 10 ml with water, and add 2 ml of diluted sulphuric acid (1 + 1) and 50 ml of acetone. Cool, and add 1 ml of dithizone solution. Titrate with silver nitrate solution until the colour of the solution begins to change to a greenish yellow. Add a further 3 ml of dithizone solution, and titrate until the solution is a clear orange-yellow colour that does not change on the further addition of silver nitrate solution.

A blank correction must be made for the silver nitrate solution needed to change the dithizone itself from green to yellow. To determine this correction, place in a 250-ml flask the reagents as before, cool, and add 4 ml of dithizone solution. Titrate from green to orange-yellow in the same way as for the sample. Four millilitres of 0·01 per cent. dithizone solution are equivalent to about 0·15 ml of 0·01 *N* silver nitrate solution.

Titration of silver with potassium iodide solution—The titration of silver with potassium iodide solution forms the basis of the titrimetric finish of the Carius digestion. In this test, the colour change is from the orange-yellow of silver keto-dithizonate to the green of dithizone. Since the green colour is more dominant than the orange-yellow, a green colour appears before all the silver dithizonate has changed to silver iodide and free dithizone. For this reason, it has been found to be better to overshoot the end-point deliberately by a small amount and then to titrate back to the orange-yellow colour with silver nitrate solution.

The procedure is as follows. By pipette, put into a 250-ml flask an aliquot of the sample solution containing about 0·05 to 0·2 milli-equivalents of silver ion. Dilute to about 10 ml with water, and add 10 ml of diluted sulphuric acid (1 + 1). (This amount of acid was used in the experimental work, as it is equal to the amount used to dissolve the silver halide in the application to the Carius method.) Cool, and add 50 ml of acetone. Add 1 ml of dithizone solution, and titrate with potassium iodide solution until a definite green colour appears. Add a further 3 ml of dithizone solution, and titrate with silver nitrate solution until a clear orange-yellow colour is again produced.

The titration value is then—

Potassium iodide titre + dithizone blank titre − silver nitrate titre.

Determine the dithizone blank correction exactly as before.

Table I

Titration of potassium iodide solution with silver nitrate solution

Amount of 0·009932 *N* potassium iodide solution taken, ml	Titre of 0·01 *N* silver nitrate solution, ml	Theoretical result, ml
5	4·976, 4·969, 4·971	4·966
10	9·933, 9·926, 9·928	9·932

TESTS OF THE METHOD—

In a check of the method for titrating iodide with silver nitrate solution, 5 and 10-ml portions of 0·009932 *N* potassium iodide solution were titrated with 0·01 *N* silver nitrate solution as described. The results are shown in Table I.

In a check of the method for titrating silver with potassium iodide solution, 5 and 10-ml portions of 0·01 *N* silver nitrate solution were titrated with 0·009932 *N* potassium iodide solution as described. The results are shown in Table II.

TABLE II

TITRATION OF SILVER NITRATE SOLUTION WITH POTASSIUM IODIDE SOLUTION

Amount of 0·01 *N* silver nitrate solution taken, ml	Titre of 0·009932 *N* potassium iodide solution, ml	Theoretical result, ml
5	5·04, 5·03, 5·04	5·036
10	10·08, 10·08, 10·075	10·072

TITRATION OF BROMIDE

The procedure for the titration of bromides is slightly different from that for iodides. It has been found that end-points are sharper if 10 ml of diluted sulphuric acid (1 + 1) are used instead of 2 ml. The problem has not been studied at such length as has the titration of iodides and chlorides. However, it has been found that accurate results can be obtained on standard solutions of potassium bromide.

TITRATION OF CHLORIDE

This method has been devised mainly for application to the determination of chloro compounds by Schöniger's adaptation[2] of Mickl and Pech's method.[3,4] It has also been shown that the method can be applied to the direct titration of microgram amounts of chloride ion.

REAGENTS—

Silver nitrate solution, 0·004 N *in* n-*propyl alcohol*—Prepared by diluting an accurately standardised 0·2 *N* aqueous solution of silver nitrate with *n*-propyl alcohol.

Dithizone solution, 0·003 *per cent. in acetone*—This solution is used for the titration of microgram amounts of chloride ion.

PROCEDURE—

(*a*) *For* 0·02 *to* 0·05 *milli-equivalent of chloride ion*—By pipette, transfer to a 250-ml flask a 1-ml portion of the sample solution containing 0·02 to 0·05 milli-equivalent of chloride ion. Add 50 ml of acetone and 0·2 ml of diluted sulphuric acid (1 + 1). Add 1 ml of 0·01 per cent. dithizone solution, and titrate with the solution of silver nitrate in *n*-propyl alcohol until the dithizone begins to change to an orange-yellow colour. Add a further 3 ml of 0·01 per cent. dithizone solution, and titrate until the solution is an orange-yellow colour. At the end-point, the addition of a further drop of titrant should produce no change in colour.

A blank correction must be deducted for the dithizone used. To determine this correction, place 4 ml of 0·01 per cent. dithizone solution in a flask containing 50 ml of acetone and 0·2 ml of diluted sulphuric acid (1 + 1), and titrate to a clear orange-yellow colour.

To standardise the silver nitrate solution, place, by means of a pipette, 1 ml of accurately standardised 0·05 *N* hydrochloric acid in a 250-ml flask, and then carry out the procedure described above.

(*b*) *For microgram amounts of chloride ion*—By pipette, transfer to a 5-ml beaker an aliquot of the sample solution containing up to 50 μg of chloride ion. If the sample is acid, make just alkaline to phenolphthalein with dilute sodium hydroxide solution. Stand the beaker in a water bath, and evaporate to dryness. Meanwhile, set up an Agla syringe-type microburette over a magnetic stirrer. Fill the burette with 0·004 *N* silver nitrate solution in *n*-propyl alcohol. Add to the beaker 0·05 ml of water, and then slowly add 1 ml of acetone, swirling the beaker when the first few drops have been added. Add 1 drop of diluted sulphuric acid (1 + 1) and 0·1 ml of 0·003 per cent. dithizone solution. Place a small glass-covered stirring bar in the beaker, and stand the beaker on the magnetic stirrer. Titrate with silver

nitrate solution from the syringe-type burette until the colour of the solution begins to change to a reddish yellow. Add 1 ml of acetone, washing down the sides of the beaker during the addition. Add 0·2 ml of 0·033 per cent. dithizone solution, and titrate to an orange-yellow colour.

Carry out a blank titration on 2 ml of acetone, 1 drop of diluted sulphuric acid (1 + 1) and 0·3 ml of dithizone solution. Deduct this value from the sample titre.

TESTS OF THE METHOD—

In a check of procedure (*a*), 1-ml portions of hydrochloric acid solutions of different concentrations were titrated with 0·004 *N* silver nitrate solution in *n*-propyl alcohol. The results are shown in Table III.

TABLE III

TITRATION OF HYDROCHLORIC ACID WITH SILVER NITRATE SOLUTION

Amount of hydrochloric acid taken, ml	Concentration of hydrochloric acid, *N*	Titre of 0·004 *N* silver nitrate solution in *n*-propyl alcohol, ml	Theoretical result, ml
1	0·01	2·50, 2·49	2·50
1	0·02	5·02, 5·01, 5·00	5·00
1	0·04	10·01, 10·01	10·00

It has been found that results of similar accuracy can be obtained by titrating with 0·01 *N* aqueous silver nitrate delivered from an Agla syringe-type microburette. Not more than 0·5 ml of titrant can be added, since, with more than 3 per cent. of water present, the sharpness of the end-point is impaired. For normal work, a solution of silver nitrate in *n*-propyl alcohol delivered from an ordinary burette is preferred, as syringe-type burettes are rather fragile.

In a check of procedure (*b*), 1-ml portions of a 0·001 *N* solution of sodium chloride were transferred by pipette to 5-ml beakers and titrated as described. The results are shown in Table IV.

TABLE IV

TITRATION OF SODIUM CHLORIDE SOLUTION WITH SILVER NITRATE SOLUTION

Amount of 0·001 *N* sodium chloride solution taken, ml	Titre of 0·004 *N* silver nitrate solution, ml	Titre less blank, ml	Recovery, %
0	0·0110	—	—
1	0·2610	0·2500	100·0
1	0·2618	0·2508	100·3
1	0·2612	0·2502	100·1
1	0·2610	0·2500	100·0

It appears that the method as described is directly applicable to the determination of chloride in tap-water. One millilitre of tap-water was transferred by pipette to a 5-ml beaker, and the titration was carried out by procedure (*b*). This gave a result of 14·2 p.p.m. of chloride ion. At the same time, 1 litre of tap-water was evaporated to a small volume and the chloride was determined by the Volhard procedure. This gave a result of 14·1 p.p.m. of chloride ion.

TITRATION OF CYANIDE

PROCEDURE—

By pipette, transfer to a 250-ml flask an aliquot of the sample solution containing up to 0·15 milli-equivalent of cyanide ion. Add 50 ml of 95 per cent. ethanol, 1 ml of *N* sodium hydroxide solution and 2·0 ml of 0·01 per cent. dithizone solution in acetone. Titrate with 0·01 *N* silver nitrate solution to a deep red-purple colour. Near the end-point the solution changes in colour from orange-yellow to a dull red, but the actual end-point is sharp and distinctive. Carry out a blank titration exactly as above, but omitting the sample, and deduct the value found from the sample titre.

At the end-point there should not be more than 20 ml of water present, including the volume of titrant added. If more water is present, the end-point is less sharp.

TESTS OF THE METHOD—

In a check of the method, an approximately 0·1 *N* solution of potassium cyanide was prepared and diluted accurately 1 + 9 with water. The cyanide content of the strong solution was determined by the Liebig method. The proposed method was carried out on different amounts of the solutions, and the results are shown in Table V.

TABLE V

TITRATION OF POTASSIUM CYANIDE SOLUTION WITH SILVER NITRATE SOLUTION

Potassium cyanide solution used	Amount of potassium cyanide solution taken, ml	Titre of 0·01 *N* silver nitrate solution, ml	Theoretical result, ml
Dilute	5	2·86, 2·88	2·87*
Dilute	10	5·72, 5·74, 5·73, 5·74	5·74*
Strong	2	11·50, 11·49	11·48†

* Calculated from the result by Liebig's method. † Result obtained by Liebig's method.

APPLICATION OF THE METHOD—

The method has been applied to the determination of traces of cyanide in acrylonitrile. In a series of tests, a 0·1 *N* solution of potassium cyanide was standardised by the Liebig method and then diluted 1 + 9. Various amounts of this dilute solution were added to 1-ml portions of pure acrylonitrile, and the proposed procedure was carried out. The results are shown in Table VI.

TABLE VI

TITRATION OF SMALL AMOUNTS OF CYANIDE IN ACRYLONITRILE

Amount of dilute potassium cyanide solution added to acrylonitrile, ml	Titre of 0·01 *N* silver nitrate solution, ml	Calculated theoretical result, ml
0·5	0·72	0·71
1	1·42	1·42
2	2·84	2·84
3	4·25	4·26
4	5·67	5·68
5	7·08	7·10

TITRATION OF SILVER WITH CYANIDE SOLUTION

REAGENTS—

Potassium cyanide solution, about 0·025 N—A solution of 1·7 g of analytical-reagent grade potassium cyanide in water made up to 500 ml.

Potassium hydroxide solution—A solution of 40 g of potassium hydroxide in water made up to 100 ml.

PROCEDURE—

By pipette, transfer to a 250-ml flask an aliquot of the sample solution containing up to 0·20 milli-equivalent of silver ion. Add 0·5 ml of ammonia solution, sp.gr. 0·880, and 1 ml of potassium hydroxide solution. Add 50 ml of 95 per cent. ethanol and 2·0 ml of 0·01 per cent. dithizone solution in acetone. Titrate with the potassium cyanide solution from a 10-ml burette until the solution changes from red to orange-yellow. Note the burette reading, and then titrate from a 10-ml burette with 0·01 *N* silver nitrate until the solution is a deep red-purple. Note the burette reading. Carry out a blank titration on the reagents with 0·01 *N* silver nitrate to the red-purple colour.

To standardise the potassium cyanide solution, repeat the procedure on 2 ml of accurately standardised 0·1 *N* silver nitrate.

Calculate the factor, *F*, of the potassium cyanide solution from the following equation—

$$F = \frac{[20{\cdot}00 + \text{silver nitrate titre, ml} - \text{reagent blank value, ml}] \times 0{\cdot}01}{\text{Potassium cyanide titre, ml}}$$

The titration value of the sample can then be calculated in ml of 0·01 *N* titrant from the following equation—

$$\text{Net titration} = \frac{\text{Potassium cyanide titre, ml} \times F - \text{silver nitrate titre, ml} + \text{reagent blank value, ml}}{0{\cdot}01}$$

TESTS OF THE METHOD—

To check the validity of the method, four 1-ml and four 2-ml portions of 0·1 *N* silver nitrate solution were titrated with potassium cyanide solution, and, from the results, the factor of the potassium cyanide solution was calculated. The results with the 1-ml portions of 0·1 *N* silver nitrate solution were 0·02272, 0·02278, 0·02272 and 0·02275, and with the 2-ml portions, 0·02273, 0·02278, 0·02275 and 0·02274.

The additions of ammonia solution and potassium hydroxide solution were made in order to reproduce the conditions that were found to be suitable for dissolving a precipitate of silver chloride from a Carius digestion. If the problem in hand was simply the determination of a soluble silver salt, almost certainly only a small amount of alkali would be necessary, as in the titration of cyanide, but this has not been confirmed by experiment.

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS AFTER DIGESTION BY THE CARIUS METHOD

Although the Carius method for halogens is the method preferred by many analysts, one of the main drawbacks is the gravimetric finish. Titrimetric finishes for bromide and iodide have been suggested.[6,7] These methods are potentially dangerous, as the tubes are handled outside the furnace after digestion. In the proposed methods, the sample is digested in the normal way in the presence of silver nitrate. After digestion, the precipitate of silver halide is washed and either dissolved in concentrated sulphuric acid and then determined by the potassium iodide titration procedure, or it is dissolved in ammonia solution, sp.gr. 0·880, and then determined by the potassium cyanide titration procedure. The sulphuric acid solution method can be applied to chlorides, bromides and iodides, but the ammonia solution method can only be applied to chlorides.

APPARATUS—

To separate the silver halide, a filter-stick similar to the well known Emich filter-stick is used. A piece of glass tubing about 16 cm long, 3 mm internal diameter and 5 mm external diameter is used for its construction. About 0·5 cm from one end, the tube is constricted to about 1·5 mm internal diameter. For use, glass-wool is pushed into the constricted end and cut off level with the end of the tube. Suction is applied and the stick is dipped in a slurry of prepared Gooch asbestos, so that a pad of asbestos is formed over the glass-wool.

PROCEDURE—

General preliminary treatment—Take sufficient sample to give an equivalent of 0·1 to 0·2 milli-equivalent of halide ion and digest in the usual way in a sealed tube with fuming nitric acid and silver nitrate. Transfer the contents of the tube to a 250-ml conical flask. If chlorine is being determined, wash the tube with a little concentrated ammonia solution, swirl to dissolve the precipitate of silver chloride, and then re-precipitate by adding concentrated nitric acid. Coagulate the precipitate by standing the flask, protected from light, in a boiling-water bath for 20 minutes. Cool the flask, and, with the filter-stick, remove the supernatant liquid. Wash twice with dilute (about 0·1 *N*) nitric acid. Remove the filter-stick from the suction line, and push a stainless-steel wire down it to dislodge the glass-wool and asbestos pad into the 250-ml flask. The sample is now ready for further treatment, the form of which will depend on whether chlorine, bromine or iodine is present and whether the sulphuric acid or ammonia method of dissolution is to be used.

Determination of chlorine and iodine by sulphuric acid treatment—Stand the flask on a water bath until the small amount of liquid adhering to the glass-wool and asbestos has evaporated. Add 5 ml of concentrated sulphuric acid, and stand the flask on a hot-plate so regulated that the sulphuric acid gently boils. Maintain at the boiling-point for 30 minutes. Cool the flask, add 15 ml of water, cool again, and add 50 ml of acetone. Complete the determination as described for the titration of silver with iodide solution on p. 572.

Determination of bromine by sulphuric acid treatment—It has been found to be difficult to dissolve silver bromide directly with hot sulphuric acid. Also, after dissolution, there

is usually present an oxidising substance (probably bromate), which oxidises the dithizone and makes the titration method inapplicable. However, this can be overcome as follows.

To the washed precipitate of silver bromide in a 250-ml flask, add 0·4 g of analytical-reagent grade potassium iodide and about 0·5 ml of water. Swirl to dissolve the potassium iodide and thoroughly moisten the precipitate of silver bromide. The silver bromide either dissolves completely or is converted into a curd-like precipitate of silver iodide. Add 5 ml of concentrated sulphuric acid, and proceed exactly as for the determination of chloride. Iodine is given off; normally it is completely expelled in about 10 minutes.

Determination of chlorine by dissolution in aqueous ammonia—This is the method of choice for the determination of chlorine, since the rather lengthy heating with sulphuric acid is avoided.

To the washed precipitate of silver chloride in a 250-ml flask, add 0·5 ml of ammonia solution, sp.gr. 0·880. Swirl to dissolve the precipitate, and then complete the determination as described for the titration of silver with cyanide solution on p. 575.

RESULTS—

A wide range of substances has not been examined, as the Carius digestion procedure is considered extremely reliable. Since the method was shown to give good results with the substances examined, it should work on all substances that are completely oxidised in the Carius digestion. The sample of poly(vinyl chloride) used in the tests was extremely pure; several replicate tests by the macro Parr bomb method gave the theoretical result of 56·8 per cent. of chlorine. The results obtained are shown in Table VII.

TABLE VII

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS AFTER CARIUS DIGESTION

Substance	Halogen found, %	Theoretical halogen content, %
By sulphuric acid treatment—		
Poly(vinyl chloride) ..	56·6, 56·8, 56·6, 56·8	56·8
Bromobenzene	50·7, 50·8	50·8
Iodobenzoic acid	51·1, 51·2, 51·3, 51·1	51·1
By dissolution in aqueous ammonia—		
Poly(vinyl chloride) ..	56·6, 56·7, 56·8, 56·7	56·8

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY A MODIFIED FORM OF SCHÖNIGER'S ADAPTATION OF MICKL AND PECH'S METHOD

Schöniger's adaptation, direct combustion in a flask in an atmosphere of oxygen, is undoubtedly one of the most rapid and convenient methods devised for the determination of halogens in organic compounds. The method can be used only on compounds that do not volatilise at room temperature.

By using the proposed method of absorption and titration, considerably less working time is involved than in the original method.

The apparatus is a somewhat modified form of that used in Schöniger's original adaptation. The sample is wrapped in filter-paper and supported in the combustion flask on a small platinum platform. The sample is fired by means of a hot Pyrex-glass rod. The chlorine evolved is absorbed in a small volume of water saturated with sulphur dioxide. Sulphur dioxide does not interfere in the direct titration of chlorides, so that no after-treatment of the sample before titration is necessary.

The method has been applied to poly(vinyl chloride), poly(vinylidene chloride) and their copolymers with various other substances. It has been found that the method is not of completely general application; some substances evolve a lot of unburnt carbon during combustion. This makes titration difficult, and invariably in such instances the results for chlorine are low. However, the method has, in practice, proved to be extremely useful for substances to which experiment has shown it to be applicable. A large number of samples can be dealt with in much less time than by any other method.

APPARATUS—

The apparatus used is as shown in Fig. 1. The vessel is a thick-walled 500-ml Quickfit and Quartz flask with a B34 standard neck. The platinum platform is about 2 cm × 1·3 cm.

A few holes are punched in it to facilitate the passage of oxygen during combustion The platform is annealed to the two glass rod supports, which are in turn sealed on to a B24 - B34 expansion cone. The firing rod is attached to a B24 cone. The end of the rod is arranged to come about 0·5 cm above the platform when fitted in position.

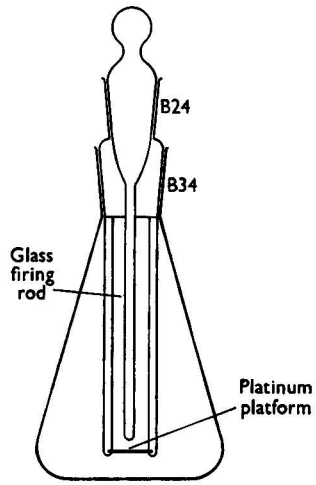

Fig. 1. Combustion apparatus

PROCEDURE—

To weigh out the sample, take a piece of Whatman No. 40 filter-paper cut out to form a rectangle about 3 cm × 4 cm. Fold the paper in three along the shorter side, so that the centre section lies flat with the other sections standing up at right angles. When handling the paper use tweezers and a flat spatula, since chlorides can be introduced from the fingers, particularly during hot weather. Transfer the paper to a microbalance, and weigh. Place 4 to 8 mg of sample centrally on the filter-paper, and re-weigh. Remove from the balance, and fold the filter-paper, applying pressure with the spatula so that the sample is wrapped tightly in several thicknesses of paper. During abnormal weather conditions, when there has been a great change in humidity over a short period, it has been found that filter-paper cannot be weighed to constant weight. This can be overcome by placing the paper in the balance case for a short while before weighing.

Take one of the thick-walled 500-ml flasks and blow a steady stream of oxygen into it for a few seconds. Add 0·5 ml of water saturated with sulphur dioxide from a siphon. Place the wrapped sample on the platinum platform, and moisten round the B34 cone with a drop of water. Lower the cone and platform in position in the flask. Take the firing rod and moisten with a drop of water round the B24 cone. Heat the end of the rod to glowing red heat in a blowpipe flame and lower into the flask so that it touches and fires the sample. While the sample is burning, hold down the firing rod. Set the flask aside for 1 hour before starting the titration procedure. No experiments have been carried out to determine the minimum time needed for complete absorption of the chlorine evolved, but experiment has shown that 1 hour is adequate. It is probable that absorption takes place almost entirely on the droplets of water that condense on the sides of the flask.

After the flask has stood for 1 hour, loosen the joints, and wash down with 50 ml of acetone from a small wash-bottle. Add 0·2 ml of diluted sulphuric acid (1 + 1), and titrate with 0·004 *N* silver nitrate solution in *n*-propyl alcohol as described for the titration of chlorides on p. 573.

It is advisable to carry out a blank determination on a piece of filter-paper the same size as that used in the determination. For some batches of filter-paper, a blank value of the order of 0·1 ml of 0·004 *N* silver nitrate solution has been found.

RESULTS—

The method was applied to the determination of chlorine in poly(vinyl chloride) and an experimental copolymer. The results are shown in Table VIII.

TABLE VIII

DETERMINATION OF CHLORINE IN ORGANIC COMPOUNDS AFTER COMBUSTION IN OXYGEN

Substance	Chlorine found, %	Theoretical chlorine content, %
Poly(vinyl chloride) ..	56·8, 56·7	56·8
Experimental copolymer ..	22·2, 22·1, 22·3, 22·3	22·2*

* Determined by the Carius method.

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Nomograms for Calculating and Testing the Morton and Stubbs Correction in the Spectrophotometric Assay of Vitamin A

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Two nomograms (for vitamin-A alcohol in *iso*propyl alcohol and for vitamin-A acetate in absolute ethanol) are given for the rapid application of the Morton and Stubbs correction without numerical calculation.

The Morton and Stubbs correction sometimes leads to erroneous results, and a practical test for the reliability of $E_{corr.}$ is proposed. The test can be carried out in a few minutes by using nomograms, and makes it possible to ascertain whether or not the irrelevant absorption is approximately linear over the wavelength range between the two fixation points at six-sevenths.

THE Morton and Stubbs correction procedure[1] in ultra-violet absorption assay of vitamin A has been widely adopted as an official method. The use of the correction is reported by International,[2] British[3] and American[4] Pharmacopoeias, as well as by the Istituto Superiore di Sanità,[5] the Association of Vitamin Chemists[6] and the Association of Official Agricultural Chemists[7] in their treatises on analysis.

The procedure involves measurement of extinction, E, at the wavelength of maximum absorption of the pure vitamin and at two other wavelengths at which E for the pure vitamin is exactly six-sevenths of $E_{max.}$ The irrelevant absorption is then subtracted from the gross value of $E_{max.}$ by means of the Morton and Stubbs equation to give $E_{corr.}$

As conventionally calculated, the Morton and Stubbs correction is tedious and time-consuming. Several simplifications of the mathematics have been proposed, based on numerical Tables, graphical procedures or a combination of both. Examples of the first type are the simplified formulae of Prokhovnik[8] and Korr[9] and the Tables of Rogers[10]; the geometrical development of Vignau[11] exemplifies the second type of simplification, and the combined calculations and nomograms of Oser[12] and McGillivray[13] are examples of the third type.

The proposed nomograms make it possible not only to apply the Morton and Stubbs correction rapidly and without numerical calculation, but also to check, in a few minutes, the reliability of $E_{corr.}$

We found it to be necessary to evolve a suitable routine test, because, during our work on the stability of some water-soluble preparations of vitamin A, the Morton and Stubbs correction often led to erroneous results. For example, $E_{corr.}$ was sometimes greater than $E_{max.}$, and, in some instances, the value of $E_{corr.}$ increased during storage.

The validity of the Morton and Stubbs geometrical correction procedure depends on the assumption (which cannot be tested experimentally[14]) that the irrelevant absorption at the fixation points is linearly related. There was good reason to believe that this assumption

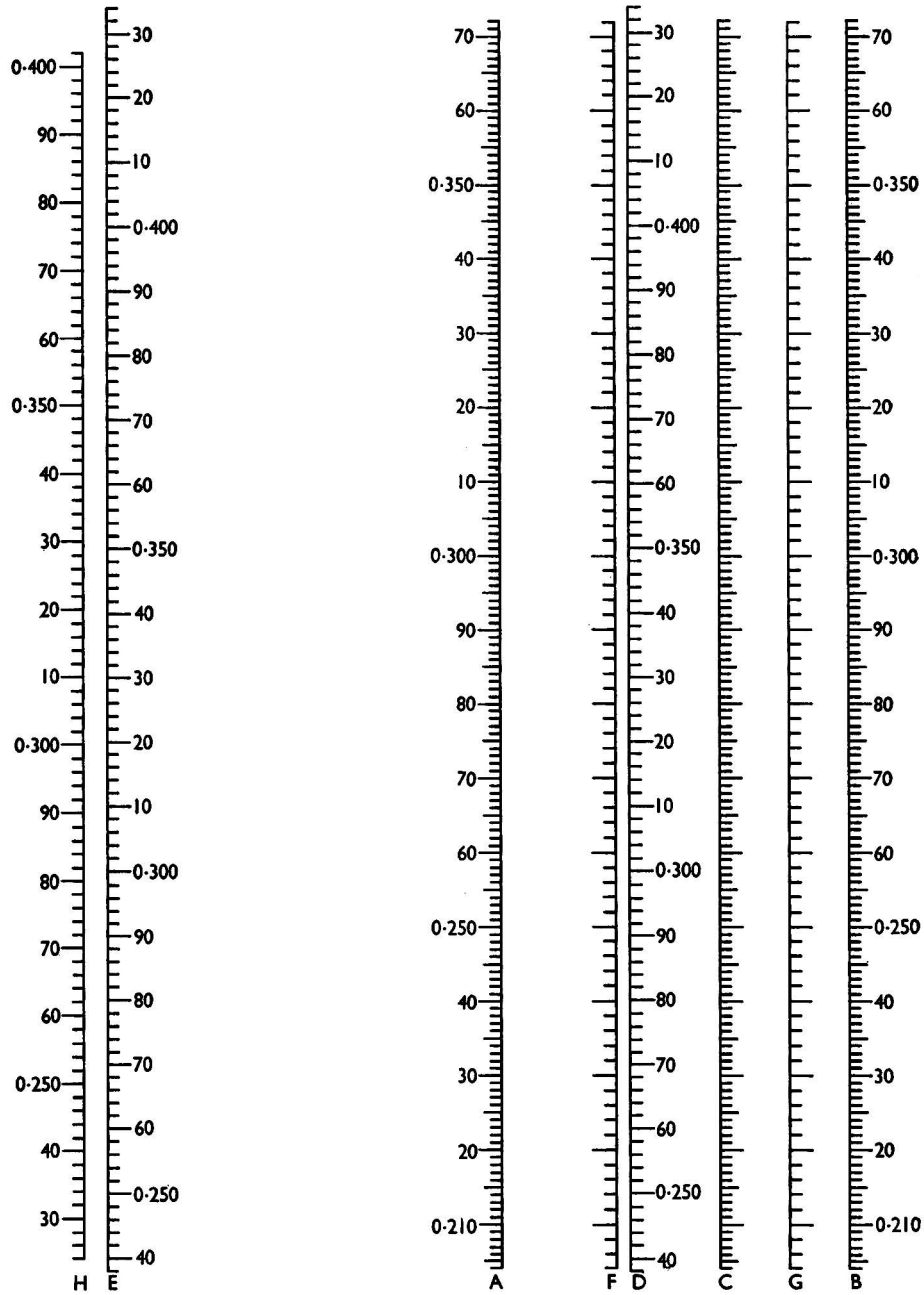

Fig. 1. Nomogram for vitamin-A alcohol in *iso*propyl alcohol

was invalid, as irrelevant-absorption curves derived geometrically[15] were not smooth between the fixation points. (In most instances for which we obtained unreliable results, the curves showed marked peaks and troughs.)

Further, it is impossible in routine work to apply the correction procedure if the sixteen wavelengths proposed by Cama, Collins and Morton[16] are used, as the procedure is too laborious.

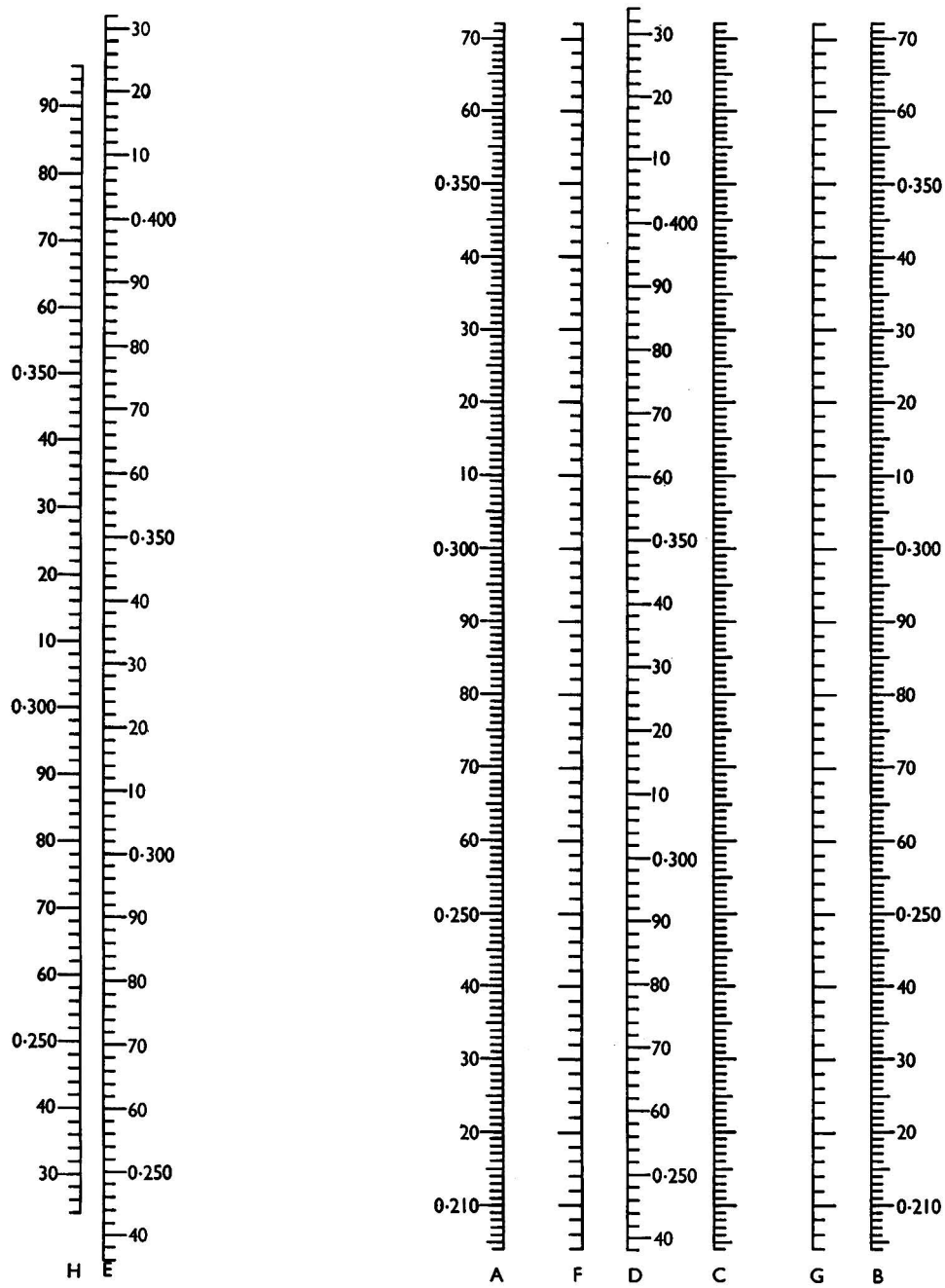

Fig. 2. Nomogram for vitamin-A acetate in absolute ethanol

Fig. 1 shows the nomogram for vitamin-A alcohol in *iso*propyl alcohol, and Fig. 2 shows that for vitamin-A acetate in absolute ethanol. We used the data of Cama, Collins and Morton[17] for ultra-violet absorption of pure all-*trans* vitamin A.

Fig. 1 is based on the more commonly used equation—

$$E_{corr.} = 7\ (E_{325} - 0{\cdot}375E_{310} - 0{\cdot}625E_{334}) \quad .. \quad .. \quad .. \quad (1)$$

which pre-supposes that $E_{310} = E_{334} = 0{\cdot}857E_{325}$ for all-*trans* vitamin-A alcohol, although the values given by Cama, Collins and Morton are a little different.

The applicability test requires the measurement of extinction at 318 and 330 mμ, at which wavelengths the coefficients of Cama, Collins and Morton are 0·932 and 0·935, respectively. For simplicity, both these were made equal to 0·935, and, by using this value, we derived the following equation—

$$E_{corr.} = 15{\cdot}385\ (E_{325} - 0{\cdot}417E_{318} - 0{\cdot}583E_{330}) \quad .. \quad .. \quad .. \quad (2)$$

Fig. 2 is based on Cama, Collins and Morton's equation—

$$E_{corr.} = 7\ (E_{326} - 0{\cdot}432E_{311{\cdot}5} - 0{\cdot}568E_{337}) \quad .. \quad .. \quad .. \quad (3)$$

For the applicability test we chose 317 and 333 mμ, at which the extinctions are both equal to $0{\cdot}924E_{326}$. For convenience, the factor 0·924 was decreased to 0·923, and, by using this value, we derived the following equation—

$$E_{corr.} = 13\ (E_{326} - 0{\cdot}4375E_{317} - 0{\cdot}5625E_{333}) \quad .. \quad .. \quad .. \quad (4)$$

Each nomogram is composed of eight parallel straight lines, A, B, C, D, E, F, G and H; A, B, C, D and E are used to find the value of $E_{corr.}$, and F, G and H are used for the applicability test. Three different scales are used; one for A, B, C, F and G, another for D and E and a third for H. The figures on lines A, B, C, D, F and G of Fig. 1 represent extinction values at wavelengths 310, 334, 325, 318 and 220 mμ, respectively. Similarly, the figures on lines A, B, D, F and G of Fig. 2 represent extinction values at wavelengths 311·5, 337, 326, 317 and 333 mμ, respectively. The figures on line C represent ($0{\cdot}375E_{310}$ + $0{\cdot}625E_{334}$) on Fig. 1 and ($0{\cdot}432E_{311{\cdot}5}$ + $0{\cdot}568E_{337}$) on Fig. 2. Line E, on both Fig. 1 and Fig. 2, gives the values of $E_{corr.}$ Line H gives $0{\cdot}935E_{corr.}$ on Fig. 1 and $0{\cdot}923E_{corr.}$ on Fig. 2.

Directions for the use of Fig. 1 are given below; the procedure for Fig. 2 is the same.

Use of nomograms

Determination of $E_{corr.}$—

If a_1, b_1 and d_1 are the extinction values at wavelengths 310, 334 and 325 mμ, respectively, a line on the nomogram from a_1 to b_1 intersects line C at c_1. The continuation of a second line from c_1 to d_1 intersects line E at a point that corresponds to the value of $E_{corr.}$.

We often found that application of the Morton and Stubbs correction resulted in a value for $E_{corr.}$ that was greater than that of $E_{max.}$. In such instances, c_1 lies below d_1 on the nomogram, and it is pointless to continue the determination of $E_{corr.}$ by the Morton and Stubbs procedure.

Applicability test—

The two fixation points at six-sevenths chosen by Morton and Stubbs do not have a true chemical significance. Morton and Stubbs[1] remark that the "only significance of the 6/7 ratio is that it is empirically appropriate in relation to the wavelength range covered, and to the performance of the spectrophotometer." Gridgeman[18] applied three different sets of fixation points (as well as those at 6/7) to the absorption data of five vitamin samples described and discussed by Adamson, Elvidge, Gridgeman, Hopkins, Stuckey and Taylor,[19] and pointed out that "except perhaps for cod-liver oil, where there is some chemical evidence for the suitability of the 6/7 points, there is nothing on which to base a decision as to which of the four sets of fixation points is best."

From these considerations, we concluded that, in general, if at least one set of suitably chosen fixation points gives values close to the values at 6/7, the Morton and Stubbs correction is more likely to be valid. If, on the other hand, the values of $E_{corr.}$ are far apart, there is no reasonable basis for application of the Morton and Stubbs correction, which, therefore, is not reliable.

This reasoning led us to substitute the slope of the curve between the two 6/7 points (in practice, a near-linearity) for the linearity of three fixation points. This assumption is closer to the basic principle of the Morton and Stubbs correction. In fact, Morton[20] writes: "The assumption is made that the irrelevant absorption is linear over the narrow wavelength range chosen." It is a purely mathematical requirement, not acceptable from the chemical

standpoint, to ask for—"specifically the linearity of three points; the absorption in between these chosen points may vary irregularly"[21]: "the contour of the curves between and beyond these points being immaterial."[18]

The assumption that the irrelevant-absorption curve is approximately linear limits the instances in which the Morton and Stubbs correction can be applied. If this assumption, however, can be verified, values of $E_{corr.}$ will have a greater degree of validity for vitamin A preparations of any type. Further, the assumption can be tested, both by a geometrical procedure[15] and by calculating sets of equations of the Morton and Stubbs type, based on different sets of fixation points in the wavelength range between the 6/7 points.

By means of the applicability test, it is possible to ascertain whether or not two intermediate subsidiary points are linearly related to three Morton and Stubbs fixation points, *i.e.*, to ascertain the near-linearity of the irrelevant-absorption curve with sufficient accuracy. Our test, therefore, is not exact, but it is rapid and sufficiently accurate for practical purposes.

The applicability test requires two subsidiary readings at 318 and 330 mμ. These two wavelengths fall almost midway between Morton and Stubbs's first fixation point and $\lambda_{max.}$, and between $\lambda_{max.}$ and Morton and Stubbs's second fixation point, respectively. The test is applied in the following manner.

$E_{corr.}$ is first determined as described previously, and the value of h_1, the point on line H that corresponds to $E_{corr.}$, is noted. The differences, $(E_{318} - h_1)$ and $(E_{330} - h_1)$, are then calculated. (These differences are m and n, respectively.)

The line joining points a_1 and b_1 intersects lines F and G at f_1 and g_1, respectively. The point d_2 on line D that corresponds to the value of $E_{corr.}$ is noted, and the two points are joined by a single straight line, which intersects line F at point f_2.

If the irrelevant-absorption curve is approximately linear, m will be equal to $(f_1 - f_2)$ and n will be equal to $(g_1 - f_2)$. Small differences in these equalities do not invalidate the applicability of the Morton and Stubbs correction.

An alternative procedure is to calculate equation (2) for the nomogram in Fig. 1 or equation (4) for the nomogram in Fig. 2. If the values of $E_{corr.}$ so determined are sufficiently close to those obtained by solving equations (1) and (3), respectively, the Morton and Stubbs correction will be reliable. This procedure is, however, time-consuming.

Extension of use of nomograms—

Determination of $E_{corr.}$ is also possible for extinction readings that are not included on the nomograms. The readings must be multiplied or divided by a suitably chosen factor, *i.e.*, one that brings extinction values within the range covered by the nomograms. Obviously, the resulting $E_{corr.}$ must be divided or multiplied by the same factor. The same procedure can be applied to the applicability test.

Results and conclusions

We have determined $E_{corr.}$, both with the nomograms and by means of the Morton and Stubbs equation, in a number of instances. Differences between the two sets of values for $E_{corr.}$ averaged $\pm 0{\cdot}002$. Skilful use of the nomograms can consistently keep the error within the same range.

The use of nomograms of the proposed type is not limited to the analyses described. It is easy to construct similar nomograms for all ultra-violet analyses of vitamin A, *e.g.*, in *cyclo*hexane, and also for those instances in which application of equations of the Morton and Stubbs type is required.

We consider it to be unnecessary to report here the mathematical calculations[22] on which our nomograms are based.

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Notes

DETERMINATION OF CALCIUM IN BIOLOGICAL MATERIAL

THE disadvantages in the determination of calcium in biological fluids by precipitation as oxalate and titration with potassium permanganate are now generally recognised. MacIntyre[1] has shown that significant losses of oxalate occur during the washing of the precipitate, and there may also be an error owing to co-precipitation of magnesium. Further, dilute permanganate solutions are not stable and the end-point is not easy to discern. Direct titration with ethylenediaminetetra-acetic acid (EDTA) has formed the basis of several methods for the determination of calcium in serum. Here again there are difficulties in recognising the end-point of the titration, especially with indicators specific for calcium, such as murexide. Also, the high pH may cause precipitation of calcium phosphate, which will necessitate a slow titration to allow the insoluble phosphate to react completely with EDTA. Better end-points have been reported by using a calcein - thymolphthalein indicator.[2,3] However, Körbl and Vydra[4] found that calcein itself did not, in fact, give any colour changes with metal ions, but only fluorescence changes. Moreover, special precautions have to be taken to avoid interference arising from the presence of large proportions of magnesium.[2] Such conditions may obtain in urine. Some of the difficulties in recognising the end-point with these indicators may be due to the presence of heavy metals in the samples.[5]

Better results should be obtained by precipitating the calcium as oxalate, dissolving the precipitate in acid and then titrating with EDTA. Davidsson,[6] who used a method of this type, endeavoured to improve the colour change at the end-point by using as indicator an Eriochrome black T solution containing small amounts of magnesium. When all the calcium had been chelated, there was a sharp colour change, owing to the formation of the magnesium - dye complex. Nielsen[7] introduced the idea of dissolving the precipitated oxalate in excess of EDTA and titrating back with a standard magnesium solution. The proposed method is based on this principle. It is readily applicable to all biological fluids and to the ashed samples of faeces, tissues and foods.

METHOD

REAGENTS—

Ammonium oxalate - oxalic acid buffer solution, pH 5·0—A solution of 6·75 g of ammonium oxalate and 0·315 g of crystalline oxalic acid in water made up to 500 ml.

Hydrochloric acid, 0·2 N.

EDTA stock solution, 10 *milli-equivalents per litre*—A solution of 1·861 g of disodium ethylene-diaminetetra-acetate dihydrate in water made up to 1 litre.

Ethanolamine, purified—The "Organic Reagent for Organic Analysis" grade, obtained from Hopkin and Williams Ltd., was used.

Standard magnesium stock solution, 50 *milli-equivalents per litre*—A solution of 1·3405 g of analytical-reagent grade magnesium acetate tetrahydrate in water made up to 250 ml. This solution should be stored in a Pyrex-glass bottle.

Indicator solution—A solution of 25 mg of Eriochrome black T in 25 ml of 2-methoxyethanol. This solution is stable at room temperature for 3 to 4 weeks.

EDTA - ethanolamine reagent solution—A mixture of 3 ml of ethanolamine and 50 ml of EDTA stock solution diluted to 100 ml with water. This solution should be prepared at frequent intervals, *i.e.*, every 2 or 3 weeks.

Standard magnesium working solution, 5 milli-equivalents per litre—Ten millilitres of standard magnesium stock solution diluted to 100 ml with water. This solution should be prepared at frequent intervals.

STANDARDISATION OF EDTA STOCK SOLUTION—

By pipette, 2·0 ml of EDTA - ethanolamine reagent solution are placed in a 15-ml centrifuge tube and 5 drops of indicator solution are added. The solution is titrated with standard magnesium working solution from a microburette until the indicator changes sharply from blue to red. Two millilitres of standard magnesium working solution should be required, and, if necessary, the EDTA stock solution should be adjusted to give this titre.

PROCEDURE—

Ashed samples of faeces, tissues or foods are dissolved in small amounts of hydrochloric acid. The solutions are diluted with water and the pH is adjusted to about 5·0 with 0·5 *N* sodium hydroxide before being made up to a suitable known volume. One-millilitre portions of these solutions or of biological fluid (serum, urine or cerebrospinal fluid) are added to 2 ml of ammonium oxalate - oxalic acid buffer solution in centrifuge tubes. For dilute urines, enough sample is used to give an adequate calcium precipitate. The contents of the tubes are mixed and the tubes are set aside for 30 minutes; they are then spun in a centrifuge for 5 minutes (3000 **g**), after which the supernatant layers are carefully poured off and saved for the determination of magnesium if necessary. Each tube is allowed to drain on filter-paper and then the precipitates are dissolved in 1-ml portions of 0·2 *N* hydrochloric acid. A 2-ml portion of EDTA - ethanolamine reagent solution and five drops of indicator solution are added to each and the mixtures are titrated with the standard magnesium working solution until the colour changes from blue to red. With urine or other specimens in which the calcium value is high, a turbidity may form when the 2·0 ml of EDTA - ethanolamine reagent solution are added. This is caused by the precipitation of excess of calcium by the base, and can be overcome by adding further 2·0-ml portions of EDTA - ethanolamine reagent solution until the precipitate has dissolved. The determination can then be completed.

CALCULATION—

The amount of calcium present is calculated from the equation—

$$\text{Calcium present, milli-equivalents per litre} = (2 - T) \times 5,$$

where T is the titre of standard magnesium working solution in millilitres.

If more than 2 ml of EDTA - ethanolamine reagent solution are required, the total volume used must be substituted for 2 in the above equation.

RESULTS

The precipitation is carried out at pH 5·0 in order to avoid the co-precipitation of magnesium.[8] Ethanolamine, as used by Sobel and Hanok,[9] was found to be a more satisfactory buffer than an ammonium hydroxide - ammonium chloride buffer solution. At the concentrations recommended, the pH of the final solution is 10·0, which Schwarzenbach[10] has shown to be the optimum for the colour change of Eriochrome black T with magnesium. We found it easier to dissolve the precipitated oxalate in dilute acid than to try dissolving it directly in the EDTA solution.

TABLE I

RESULTS OF RECOVERY EXPERIMENTS

Calcium added, milli-equivalents per litre	Magnesium added, milli-equivalents per litre	Calcium calculated, milli-equivalents per litre	Calcium found, milli-equivalents per litre	Mean recovery, %
—	—	—	4·7, 4·7*	—
0	0	—	4·65, 4·7	—
0	5·0	—	4·7, 4·65	—
1·0	4·0	5·68	5·60, 5·7	99·4
2·0	3·0	6·68	6·65, 6·7	99·7
3·0	3·0	7·68	7·7, 7·7	100·5
4·0	2·0	8·68	8·60, 8·7	99·6
5·0	2·0	9·68	9·7, 9·7	100·5
6·0	1·0	10·68	10·6, 10·7	99·8
7·0	0	11·68	11·8, 11·7	101·0

* Results for the direct determination in serum.

In order to test the specificity of the method and the recovery of calcium from serum, a series of solutions containing the proportions of calcium and magnesium shown in Table I was prepared. To 1-ml portions of a pooled serum were added 1 ml of each of these solutions and then 2 ml of ammonium oxalate - oxalic acid buffer solution; the determination of calcium was then completed by the proposed method. The results in Table I indicate that calcium is cleanly and quantitatively precipitated, even in the presence of large amounts of magnesium.

The reproducibility of results by the method is good. In a series of 50 analyses, including those quoted in Table I, the standard deviation of the differences between duplicate results, expressed as a percentage of the mean value, was ± 1 per cent. As a further check on the reproducibility of results by the method, samples of the same serum were analysed in duplicate by five different analysts in three different laboratories, the results being as follows—

Analyst No.	1	2	3	4	5
Mean calcium found, milli-equivalents per litre	5·2	5·4	5·1	5·2	5·3

The method is rapid, since no washing of the calcium precipitate is necessary and the final titration can be carried out quickly. A further advantage is that over-titration can easily be corrected by addition of more EDTA - ethanolamine reagent solution and continuation of the titration. We have been using 1-ml samples for the routine analysis of serum and cerebrospinal fluid, because we determine magnesium in the supernatant liquid after the precipitation of calcium. If only calcium is required, 0·5 ml of serum can be used in the proposed method. Finally, the method could readily be adapted for use with other complexometric indicators that may become available.

Normal values

The mean serum calcium in a series of 17 normal adults (male and female laboratory personnel) determined by the proposed method was 4·92 milli-equivalents per litre, with a standard deviation of $\pm 0{\cdot}27$ milli-equivalent per litre.

Cerebrospinal fluids from 20 patients (children and adults), in whom investigation showed no abnormality of the central nervous system, were found to have a mean calcium content of $2{\cdot}36 \pm 0{\cdot}2$ milli-equivalents per litre. This value is in fairly good agreement with that found by other workers,[11,12] but there is a slightly wider range, owing most probably to the greater heterogeneity of our series, both in respect of age and physical condition.

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THE EFFECT OF SELECTED ORGANIC COMPOUNDS ON THE DETERMINATION OF SILICA BY THE MOLYBDENUM BLUE METHOD

The influence of inorganic materials[1,2,3] on the determination of silica by the molybdenum blue method has been extensively studied, but little work has been reported on the influence of organic materials. It was considered to be of interest, therefore, to determine the effects of some common organic materials on the colorimetric determination of silica, since the normal method of determination by evaporating to dryness, burning off the organic material and then fusing with sodium carbonate is both tedious and liable to considerable error if the amounts of silica present are small.

The colorimetric technique used was similar to that described by Prentice and Ritchie,[3] but the molybdosilicic acid was developed in a solution 0·1 *N* with respect to sulphuric acid.[4]

Results

The effects noted were classified in five groups. The first group produced a small additive effect on the amount of silica determined. This group included many of the sugars with a reducing group, *e.g.*, rhamnose, sorbose, mannose, L-arabinose and xylose. Up to 200 mg of any of these sugars, when added to a solution containing only a small amount of silica (0·1 mg), caused an error in the determination of less than 4 per cent.

The second group produced an additive effect that was followed by a decrease in the amount of silica determined. Fructose was the only substance to exhibit this behaviour.

The third group produced a depressive effect, which increased with the amount of material added, until a precipitate was formed; this group included glycine and *n*-butyric acid. It was noted that ϵ-amino-*n*-caproic acid and DL-α-amino*iso*butyric acid caused precipitation if only 100 mg were added.

The fourth group produced no effect until a certain amount of material was present, after which the amount of silica found decreased rapidly with further addition of organic matter; this group included mannitol, dulcitol, sorbitol, erythritol and gluconic acid.

The fifth group consisted of a number of compounds that had no effect on the determination of silica. These were as follows, the limiting amount of organic material investigated being shown in parenthesis—

Sucrose (2 g), inositol (500 mg), pure ethylene glycol (1 ml), succinic acid (500 mg), arabonic acid (400 mg), galactonic acid (400 mg), glutamic acid (300 mg) and glucuronic acid (200 mg).

Discussion of results

The most interesting results are those of the fourth group. The concentration of polyhydroxy compound required to produce interference was found to be independent of the silica content within the range investigated (0·05 to 0·2 mg of silica).

This silica content is, however, much less than the smallest amount of organic matter that causes interference (60 mg of mannitol). To determine the factors that cause interference, the conditions of development of the molybdosilicic acid in the presence of organic matter were examined critically. This investigation showed that the amount of polyhydroxy compound required to prevent complete formation of the molybdosilicic acid was dependent on the amount of ammonium molybdate present. If excess of ammonium molybdate was added, molybdosilicic acid development was complete even at relatively high concentrations of interfering compound.

It seemed obvious from these results that interference was caused by complex formation between the molybdic acid and polyhydroxy compound. Complex formation between molybdic acid and mannitol has been reported by Frey.[5] Complex formation between molybdic acid and the other interfering polyhydroxy compounds has been confirmed in this laboratory, conductimetric and potentiometric techniques being used.

Addition of erythritol, mannitol or gluconic acid to a fully developed solution of molybdosilicic acid had no effect on the intensity of the yellow colour, and, on reduction to molybdenum blue, the full amount of added silica was determined experimentally.

The mannitol - molybdic acid complex appears to be stronger than the erythritol complex, as molybdosilicic acid was not produced in a solution containing 120 mg of mannitol within 1 week at room temperature, whereas development of molybdosilicic acid was almost complete within 45 minutes in a solution containing 300 mg of erythritol.

The effect of fructose on the determination of silica can be readily explained, as fructose combines with ammonium molybdate in acid solution to form a blue complex.[6] A method based on this reaction has been described for the determination of small amounts of fructose.

All the amino acids examined caused appreciable interference, even in small concentrations. This may be attributed to several causes, such as complex formation between amino acids and both molybdic and molybdosilicic acid. The heteropolyacids are known to form complexes with compounds containing amino groups.

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THE DECOMPOSITION OF CYANATES IN ACID SOLUTION, WITH REFERENCE TO THE ANALYSIS OF CHROMIUM-BEARING MINERALS AND ALLOYS

IN the analysis of, *e.g.*, rocks or steels, the presence of appreciable amounts of chromium may give rise to serious errors during the hydrolytic precipitation of the hydrated oxides of group 3, owing to the formation of chromammines, such as $[Cr(NH_3)_6]^{3+}$, the hydroxides of which are soluble in solutions buffered with ammonium salts, causing incomplete precipitation of chromium. Formation of chromammines may be prevented by very slow addition of ammonia to the boiling solution, as in the elegant method of Trombe[1,2] of passing a stream of air containing ammonia gas through the solution. Or it may be avoided by slow production of ammonia in the solution by hydrolysis of a cyanate[3] (see Table I, reactions 1, 2 and 3). This method has the great advantage of increasing the particle size and filterability of the precipitate. Dupuis and Duval[2] have shown indeed that a definite hydrate can be formed. Precipitation is rapid and quantitative for all the metals of this group.

EXPERIMENTAL

When the method was applied to chromite analysis, however, it was found that the methyl red indicator added to the solution at a later stage for the determination of magnesium was destroyed. This was attributed to the presence of some decomposition product of the cyanate that possessed mild oxidising powers. Very prolonged evaporation with hydrochloric acid was necessary to remove this product before the indicator could be used. As methyl red is an azo compound, it was thought that the indicator was being attacked at the azo bond, and that other indicators of the sulphone- or phenol-phthalein type would be stable. Bromocresol green, chlorophenol red and neutral red proved to be stable and serviceable, although methyl orange—another azo compound—was destroyed.

Were this the only trouble, substitution of one of these indicators for methyl red in the established procedure would mend matters; but two further disturbing factors arise. First, during hydrolysis of the cyanate, an insoluble substance is formed, which is precipitated together with the chromium. This naturally causes errors if the mixed precipitate is weighed, but, where chromium alone is determined in the precipitate by titrimetric means, this might be assumed to be harmless, whereas there is some disturbance of the procedure and an increased scatter in the results. Second, when nickel is present, as in nichrome, or when the initial peroxide fusion is carried out in nickel crucibles, the removal of the nickel with dimethylglyoxime is rendered difficult. Decomposition products of the cyanate appear to peptise the nickel precipitate so that filtration becomes difficult, to retard precipitation so that even with a large excess of precipitant some hours are required before precipitation is complete, and to render precipitation incomplete unless a very large excess—about ten-fold—of reagent is used. This need not necessarily cause errors, but it is very inconvenient.

An investigation to determine the nature and, if possible, the mechanism of formation of these decomposition products was undertaken.

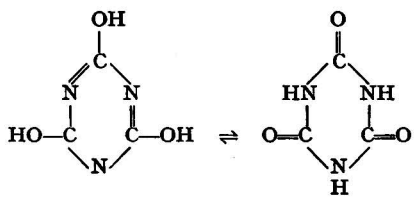
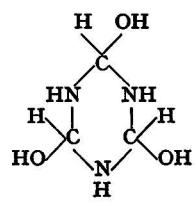
A sample of pure sodium cyanate, treated with dilute iron-free hydrochloric acid, gave an immediate white precipitate and a solution that oxidised methyl red, methyl orange, leucomethylene blue and leucosafranine-T, but did not affect neutral red, iodides or indicators of higher potential such as diphenylamine, dianisidine or erioglaucine, nor did it attack the azo bonds of magneson I or magneson II. This indicates a mild oxidant with a potential of about 0·35 to 0·40 volt, and the solution showed a potential to platinum - calomel of +0·33 volt on the hydrogen scale.

The white precipitate gave no melting point, was recrystallisable from hot water—so could not be cyamelide—was found to contain sodium and on analysis corresponded to monosodium dihydrogen cyanurate. Its oxidising powers were the same as those of the solution. Decomposition of the polymer by heating with hydrochloric acid of concentrations from 0·1 to 2·0 *M* was investigated. The decomposition was extremely slow, and was complete in 2·0 *M* acid only after boiling for 15 hours; lower acid concentrations did not appear to hydrolyse it at all. Application of various acids to the decomposition of sodium cyanate showed that hydrobromic, hydriodic, sulphuric, perchloric, phosphoric and acetic acids gave abundant precipitates of sodium cyanurate

and oxidising solutions, further decomposition being negligible. Nitric acid alone gave no polymer and no oxidising solution, although once the cyanurate had been formed it was stable to nitric acid.

TABLE I

REACTIONS DURING DECOMPOSITION OF SODIUM CYANATE

	Reaction	Remarks
1.	$NaCNO \leftrightharpoons Na^+ + CNO^-$	
2.	$CNO^- + H^+ \leftrightharpoons HCNO$	HCNO is undissociated
3.	$HCNO + H_2O \rightarrow NH_3 + CO_2$	Main reaction
4.	$NH_3 + HCNO \leftrightharpoons NH_4CNO \leftrightharpoons O{=}C(NH_2)_2$	Formation of urea
5.	$O{=}C(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$	Hydrolysis of urea
6.	$HCNO + H_2O \leftrightharpoons O{=}C(OH)NH_2 \leftrightharpoons CO_2 + NH_3$	Formation and hydrolysis of carbamic acid
7.	$2\,N{\equiv}C{-}NH_2 + 4H_2O \leftrightharpoons 2\,O{=}C(OH)NH_2 + 6H^+ + 6e$	Reduction of nitric acid
8.	$O{=}C(NH_2)_2 + H_2O \rightarrow CO_2 + N_2 + 6H^+ + 6e$	Reduction of nitric acid
9.	$2\,O{=}C(OH)NH_2 \rightarrow 2CO_2 + N_2 + 6H^+ + 6e$	Reduction of nitric acid
10.	$NO_2^- + 2H^+ + e \leftrightharpoons NO_2^- + H_2O$	Reduction of nitric acid
11.	$4\,O{=}C(NH_2)_2 + 6NO_2^- \rightarrow 4CO_2 + 7N_2 + 8H_2O$	Removal of urea
12.	$O{=}C(OH)NH_2 + NO_2^- + H^+ \rightarrow CO_2 + N_2 + 2H_2O$	
13.	$3HCNO \rightleftharpoons$ 	Polymerisation of cyanic acid
14.	$(HCNO)_3 + 6H^+ + 6e \leftrightharpoons 3HC(O)NH_2 \leftrightharpoons$ 	Possible oxidative reaction of cyanic acid polymer

Nitric acid thus apparently destroys some intermediate product necessary either as a catalyst or as a starting material for the polymerisation. Probable intermediates are urea or carbamic acid, which may be formed by reactions 4 and 6 (see Table I). This was confirmed by adding pure urea to the cyanate and nitric acid (the cyanate hydrolysis being much more rapid than the urea hydrolysis—reaction 5, Table I—at lower temperatures) when immediate formation of the polymer occurred, together with formation of an oxidising solution. The nitric acid is therefore removing urea and preventing it from catalysing the polymerisation, and this must proceed via preliminary reduction of the nitric acid to nitrous acid in some such manner as is formulated in Table I, reactions 7 to 10. This was confirmed by adding small amounts of pure sodium nitrite to samples of the acids previously enumerated. On reaction with cyanate, no polymer formation occurred, and the solutions after effervescence ceased had no oxidising powers.

The nitrite must react by removing the urea (see Table I, reaction 11), since it gives no reaction with cyanurate once this is formed, and the function of the urea must be catalytic or carrier-catalytic in the polymerisation of cyanic acid, because no polymerisation of urea alone could be effected under any conditions of concentration or temperature in hydrochloric acid and sodium chloride solutions, even in the presence of small traces of cyanate. The scheme of reactions is shown in Table I, with reaction 13 for the polymerisation of cyanic acid, and reaction 14 as a possible oxidative reaction of the polymer. Alternative reactions involving carbamic acid instead of urea are shown in the Table at 6, 9 and 12.

Method

In using cyanate for the precipitation of hydrated oxides in chromite analysis,[4] it is recommended that one of the following procedures be adopted.

(*i*) The peroxide fusion should be leached with nitric acid, the chromate reduced with sulphur dioxide and the silica dehydrations carried out with nitric acid.

(*ii*) Hydrochloric acid may be used up to the second silica dehydration, and the residue after baking extracted with nitric acid.

(*iii*) Hydrochloric acid may be used throughout, but, before adding the cyanate, a small amount of sodium nitrite should be added.

For example, in procedure (*i*), concentrate the combined filtrates and washings from the silica dehydrations to 200 to 250 ml, cool, add ammonia until a faint permanent precipitate appears, re-dissolve the precipitate with 2 ml of nitric acid, add a solution of 3 g of sodium cyanate with care to avoid loss by effervescence, heat the solution to boiling and keep at that temperature for 5 minutes. Filter on a fast-filtering paper and wash with a 1 per cent. solution of ammonium nitrate that has been neutralised to phenol red. Addition of excess of ammonia to the filtrate to recover traces of chromium[4] is not necessary provided ample sodium cyanate is used. Add excess of 1 per cent. solution of the sodium salt of dimethylglyoxime to the solution, render faintly ammoniacal, digest at just below boiling-point, filter and wash. Re-acidify the filtrate and washings with hydrochloric acid, evaporate the solution to small volume and precipitate magnesium in the usual manner.

The use of nitric acid is advantageous in that when the solution is evaporated for the determination of magnesia, the excess of ammonium salts, which are objectionable in magnesia determination, is decomposed.

Results

All three procedures have been used with success, as the results of the analyses shown in Table II indicate. Each result is the mean of three determinations, one by each of the procedures mentioned.

Table II

Results

		Cr, %	Fe, %	Si, %
U.S. Bureau of Standards Ferrochrome: Sample No. 64 ..	Given	67·9	24·05	2·05
	Found	67·8	24·1	2·1

		SiO_2, %	Cr_2O_3, %	FeO, %	MgO, %
Hoepfner Chromeisensteins:					
Sample No. X–1	Given	—	28·15	11·05	—
	Found	—	28·10	11·15	—
Sample No. XII–2	Given	—	49·73	17·25	—
	Found	—	49·9	17·19	—
Bureau of Analysed Samples					
Chrome ironstones:					
Sample No. 49G	Given	n.d.	45·05	26·4	9·24
	Found	n.d.	45·11	26·35	9·30
Sample No. 49AG	Given	3·50	49·5	13·55	16·60
	Found	3·49	49·53	13·53	16·55

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STATUTORY INSTRUMENTS*

1958—No. 1319. The Public Health (Preservatives etc. in Food) (Amendment) Regulations, 1958. Price 3d.

These amending regulations, which came into operation on August 14th, 1958, provide for the sale and importation of citrus fruit containing diphenyl or ortho-phenylphenol or mixtures of these substances within prescribed limits.

1958—No. 1454. The Antioxidant in Food Regulations, 1958. Price 4d.

These regulations, which apply to England and Wales only, and which came into operation on September 6th, 1958, permit the sale and importation of certain foods containing certain anti-oxidants within prescribed limits.

* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

FOOD STANDARDS COMMITTEE

RECOMMENDED LIMITS FOR COPPER IN FOODS

THE Minister of Agriculture, Fisheries and Food, the Minister of Health and the Secretary of State for Scotland have considered the revised Report of the Food Standards Committee on Copper, published in February, 1956 (*Analyst*, 1956, **81**, 182), and the representations subsequently received from the interests concerned. They do not propose to make any regulations under the Food and Drugs Acts prescribing these limits; the provisions relating to copper in the Food Standards (Edible Gelatin) Order, 1951, and the Food Standards (Tomato Ketchup) (Amendment) Regulations, 1956, will, however, be retained.

In the light of representations made on the revised report, the Committee have made some changes in the limits recommended for certain foods, and these are listed in Circular FSH 13/58, obtainable from H.M. Stationery Office, pride 3d. (plus postage).

Book Reviews

TRACE ANALYSIS. Edited by JOHN H. YOE, M.S., M.A., Ph.D., and H. J. KOCH, JUN., A.B., M.D. Pp. xiv + 672. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price $12.00; 96s.

This book is a collection of the papers presented at a symposium on trace analysis held in New York in November, 1955. The symposium was jointly financed by the Rockefeller Foundation and the Sloan - Kettering Institute, and the purposes of the symposium were defined as—

(*a*) To bring together for comparison and discussion authorities in the various scientific disciplines that are related to the analysis of trace constituents in industrial, agricultural, biological and medical fields.
(*b*) To consider which of the various techniques are directly applicable to the various fields of investigation.
(*c*) To discuss the separation and concentration of millimicrogram amounts of metals and contamination hazards.

The programme of the Symposium was based on three major divisions: "Methodology"; "Instrumentation"; "Separation, Concentration and Contamination Hazards." Under "Methodology," papers were given by eminent chemists on twenty different techniques. The list included R. L. Mitchell and A. A. Smales from this country on emission spectrochemical analysis and neutron-activation analysis, respectively, and, to mention only a few of the remainder, B. L. Vallee on flame spectrometry, N. H. Furman on potentiometry and L. B. Rogers on coulometry. The general standard of these contributions is high, but that of the discussions is more variable.

There are two papers under "Instrumentation," both by Ralph H. Müller, the first headed only "Instrumentation" and the other "The Interaction of Beta Particles with Matter." Dr. Müller, as always, has some stimulating things to say, and he starts his paper on instrumentation by reminding us that analytical chemistry has always depended on instruments and that "a precise analytical balance is one of the finest examples of an elegant instrument." He goes on to distinguish on the one hand between those methods in which, through the agency of modern equipment, some property other than mass is measured as the final stage of a chemical analysis and, on the other, those newer techniques, such as microwave absorption and nuclear magnetic resonance, which are of growing usefulness to the analyst and by means of which classical chemical analysis is supplanted. He asserts that, because of confused thinking on these matters, "the classical analyst is mildly infuriated by the inference that it (instrument measurement) is something new" and "the physicist and instrumentation specialist regard present-day instrumental analysis as an interim solution which is still hampered by old-fashioned thinking and practices." In the opinion of the reviewer, this confusion between measurement and analysis presents a real danger to the younger analyst, and Dr. Müller has done well to focus attention on the problem.

Of equal service is the contribution by W. W. Meinke of Ann Arbor on trace-element sensitivity. His paper deals with a number of comparisons of the results of activation analysis with those obtained by other methods—spark and arc emission spectrography, flame spectrometry, amperometric methods and "chemical" methods. Readers will be surprised to learn how often a chemical or a flame-spectrometric method is the most attractive.

The final chapter, by R. E. Thiers of the Harvard Medical School, "Separation, Concentration and Contamination," is a most fitting conclusion to the book. The author sets out in proper perspective the difficulties and hazards to which all trace analytical techniques are subject, and gives much quantitative information that is of value to the experienced analyst who is only too well aware of the difficulties that beset him and which may so seriously affect his results.

The last comment in the discussion on this paper by B. L. Vallee, and the last sentence in the book, are appropriate—"Considerations such as these, often overlooked in favour of methodology, deserve emphasis to retain our perspective with regard to the reasons for and utilisation of analytical data."

The organisers of the Symposium are to be congratulated on having made available to analysts such a valuable collection of papers.

R. C. CHIRNSIDE

ABSORPTION SPECTROPHOTOMETRY. By G. P. LOTHIAN, M.A., F.Inst.P. Second Edition. Pp. viii + 246. London: Hilger & Watts Ltd. 1958. Price 52s.

This is the second edition of a book first published in 1949. Most of the chapters have been rewritten and brought up to date, but the general plan is retained.

Part I, on the principles of spectrophotometry, reviews the early work and ably disentangles various points of terminology. The nature of absorption processes is outlined briefly. The classical laws of absorption and the problems of accuracy in spectrophotometry are reviewed in some detail and with discernment. There is an excellent chapter on calculations leading to the analysis of mixtures by either infra-red absorption or ultra-violet absorption.

Part II consists of two chapters, one on the investigation of chemical structure and chemical reaction and the other on some illustrations of the successful application of spectrophotometry to analysis.

Part III consists of six chapters on the technique of spectrophotometry. The topics dealt with include first the general principles of design of monochromators, photometers, photoelectric colorimeters, absorptiometers and spectrophotometers. Then follows an account of thermal-detector spectrophotometers and clear descriptions of some commercially available infra-red spectrophotometers. There are shorter chapters on photographic and visual spectrometers and also on cells, standards and solvents. Finally, there are useful suggestions for further reading, and a bibliography.

Mr. Lothian's emphasis is that of a physicist. The middle section of his book is a short but interesting enough essay. The first and third parts, however, are admirably planned to meet the needs of the majority of users of spectrophotometers. Most workers nowadays like to understand how the instruments work, but they find that it saves time to seek help when anything goes wrong. Indeed, much of the servicing falls to the specialist electronic technician. If this delegation allows users to devote more of their energy to the application of spectrophotometry, it need not be regretted.

R. A. MORTON

ORGANIC REACTIONS. Volume IX. Editor-in-Chief: ROGER ADAMS. Pp. viii + 468. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price $12.00; 96s.

Once again synthetic organic chemists are indebted to the Editor-in-Chief of this series and his colleagues for having collected together reliable, critical and authoritative articles on a number of useful general reactions, seven such being dealt with in this volume.

By far the longest article is that by A. C. Cope, H. L. Holmes and H. O. House on "The Alkylation of Esters and Nitriles," which forms Chapter 5 of the volume, occupies 225 pages and gives 1080 references. It deals with the first stage of that classical reaction, the malonic ester synthesis, and its relatives, treating in a masterly fashion the C-alkylation of malonic and cyanoacetic esters, malononitriles, monocarboxylic esters and mononitriles. This chapter alone will ensure that the present volume will be one of the most widely used of the whole series. Further such articles on standard classical reactions would, the reviewer feels sure, be welcomed by all organic chemists.

The other six chapters deal with rather less widely used reactions, all of which are, however, useful and welcome additions to the series. They comprise: "The Cleavage of Non-enolizable Ketones with Sodium Amide," by K. E. Hamlin and A. W. Weston, 36 pages, 96 references; "The Gattermann Synthesis of Aldehydes," by W. E. Truce, 36 pages, 109 references; "The Baeyer-Villiger Oxidation of Aldehydes and Ketones," by C. H. Hassall, 34 pages, 164 references; "The Reactions of Halogens with Silver Salts of Carboxylic Acids," by C. V. Wilson, 56 pages, 103 references; "The Synthesis of β-Lactams," by J. C. Sheehan and E. J. Corey, 21 pages, 44 references; and "The Pschorr Synthesis and Related Diazonium Ring Closure Reactions," by de L. F. de Tar, 54 pages, 225 references.

No organic chemist can afford to be without this volume or, for that matter, any of the other eight volumes of the series.

H. N. RYDON

ION EXCHANGE RESINS. By R. KUNIN. Second Edition. Pp. xiv + 466. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1958. Price $11.00; 88s.

This is more than "just a new edition" of the slim volume of the same title by Kunin and Myers that appeared in 1950. It has been considerably expanded and widened in scope, and it now comprises a comprehensive, up-to-date and well balanced survey of all aspects of the subject.

To emphasise the broad coverage of this monograph, it is worth quoting the chapter titles in full: introduction and historical review; the theory and mechanism of ion exchange; cation exchange resin characteristics; anion exchange resin characteristics; the synthesis of ion exchange resins; applications, general considerations; water softening by ion exchange; the deionization of water; ion exchange treatment of sugar and glycerine; hydrometallurgical applications; permselective membranes and their applications; catalysis with ion exchange resins; ion exchange in analytical chemistry; miscellaneous applications; methods of studying ion exchange resins; stability of ion exchange resins; the design and economics of ion exchange units.

The author is the well known expert of the Rohm and Haas Company (of Amberlite fame) and he writes authoritatively and concisely. The text is profusely illustrated with diagrams and judiciously reinforced with references—1170 of them. (Incidentally, a graph reproduced in the preface shows that already in 1955 about 1200 publications a year dealt with ion exchange—and the graph is rising steeply!)

Although the treatment of some topics is necessarily rather perfunctory, it is difficult to imagine a more informative monograph within the compass of 466 pages; as the book is also excellently produced, it can be strongly recommended for all chemical libraries.

J. A. KITCHENER

MATERIALS FOR GAS CHROMATOGRAPHY: STANDARDS AND DATA FOR "EMBAPHASE" STATIONARY PHASES AND "EMBACEL" KIESELGUHR. Published by May & Baker Ltd. Loose leaf. Pp. 23 + vi (appendix) + 7 data sheets. Dagenham: May & Baker Ltd. Gratis on application.

In the past few years a great deal of gas-chromatographic work has been carried out in which particular separations have been effected on stationary phases held on supporting media, when both phase and support have often been of uncertain composition. It is obviously desirable that workers in one part of the world should be able to repeat the work of contributors elsewhere, and hence it is no surprise that attempts should be made to standardise most of the materials used in gas chromatography In this connection the booklet fulfils a very useful purpose. Stationary

phases are described both by name and application, with useful references to the original literature. Specifications for stationary phases and supports are given in detail, and tests for the determination of volatility and retention volumes of the phases and for the catalytic activity of supports are described. There is a certain tendency to overstate the case. For example, on p. 18 the reader would be more confident about the reasoning if full details of the tests for catalytic activity of the kieselguhrs were given. Not all the references are correct. On p 9, reference 33 for dinonyl sebacate refers to the determination of methyl *cyclo*hexane in petroleum ether and not to the determination of monomers in plastics. Further, in the specifications for stationary phases, the initial loss in volatility should be given with reference to a temperature. Nevertheless, despite these blemishes, one can quote the North Country saying that "Good stuff lies in little room," for this booklet bears out the contention.

J. HASLAM

THE EXTRA PHARMACOPOEIA (MARTINDALE). Published by direction of the Council of The Pharmaceutical Society of Great Britain. Twenty-fourth Edition. Volume I. Pp. xxxii + 1695. London: The Pharmaceutical Press. 1958. Price 65s.

The original of this well known work of reference was written by William Martindale and appeared as a single volume of 313 pages in 1883. The book was an immediate success, ever larger editions being published in rapid succession, and in 1912 (when the book was being produced by the founder's son, Dr. William Harrison Martindale, with the help of Dr. W. Wynn Westcott) the fifteenth edition was issued in two volumes, the therapeutics and pharmacy of drugs being dealt with in the first volume, and the second embodying information relative to chemical analysis and general laboratory work. This arrangement has been retained, whence the volume under review is devoted to descriptions of the properties and uses of drugs and pharmaceutical preparations.

"Martindale" has become so well known as an essential work of reference to everyone whose business is in any way concerned with drugs that it would be redundant to enter into a detailed review. However, all interested readers may rest assured that this edition lives up to the fine traditions of its predecessors. As an indication, it may be mentioned that 137 closely printed pages are devoted to antibiotics, these being related to the British Pharmacopoeia 1958; again, one notices that the section dealing with Medicinal Dyes begins with a reference to the Reports on Colouring Matters of the Food Standards Committee of the Ministry of Agriculture, Fisheries and Food and the dyes have been given the five-figure numbers (whenever known) under which they appear in the "Colour Index," Second Edition, 1956. The practising analyst will find the information about proprietary preparations particularly useful, this being more detailed than in previous editions.

The magnitude of the work may conveniently be indicated by observing that the general index of 300 columns contains upwards of 18,000 references. "Martindale" is now compiled by the Scientific Publications Department of The Pharmaceutical Society of Great Britain; the Editor, Dr. K. R. Capper, the Assistant Editor, Mr. S. C. Jolly, and all the members of their staff merit high commendation for having produced this distinguished work of scientific reference.

NOEL L. ALLPORT

THE EXAMINATION OF WATER AND WATER SUPPLIES (THRESH, BEALE AND SUCKLING). By EDWIN WINDLE TAYLOR, M.A., M.D., B.Ch. (Cantab.), M.R.C.S., L.R.C.P., D.P.H. (Lond.). Seventh Edition. Pp. viii + 841. London: J. & A. Churchill Ltd. 1958. Price 100s.

When contemplating the 841 pages of the seventh edition of "The Examination of Water and Water Supplies," the conscientious reviewer may thankfully recognise that a textbook for which public demand has required seven editions and a reprint over a period of 54 years has an established place in the libraries of the world; he may fairly approach his task by endorsing the commendations of his predecessors about the main body of the work and concentrating his attention upon new matter.

Dr. Windle Taylor has wisely retained the logical arrangement that has always been an appreciated feature of the book, so that readers familiar with earlier editions can readily find their way about; but nearly every chapter in the latest edition contains something new and valuable, and room has been made by condensing and occasionally omitting some of the rather discursive accounts of individual problems that were found in earlier editions. An entirely new feature is the reproduction of sixteen plates of photomicrographs in the chapter devoted to microscopical and biological examinations. They replace the twenty-four plates of sketches which hitherto

appeared at the end of the book, and the change has sacrificed something of value. The non-expert microscopist will not usually find in his field of vision the clarity of micro-organisms in pure culture; the deposits he surveys will more frequently consist of encysted infusoria, zoogloea, fragments of quartz, larvae and the wing cases of insects, vegetable debris and sometimes textile fibres. The older sketches, with their accompanying explanations, were helpful aids to the recognition and identification of "settleable solids": the new photomicrographs, excellent of their kind though they undoubtedly are, are not wholly adequate substitutes.

Many readers will turn early to the chapter on radioactivity in water. They will find no guidance on the selection and use of testing equipment and only outlined proposals for separating radioactive material into its physiologically important components; but the author presents, in an admirably concise way, much information about background activity, proposed limits for radioactivity in water supplies, methods of calculating and expressing radioactivity and similar aspects of this new and rather intimidating subject of special interest to the water examiner. The references from which much of the information is extracted are clearly given at the end of the chapter.

A new chapter describes non-routine bacteriological examinations relating to many technical problems. Within a few pages the author includes much theoretical and practical information on the isolation, identification, significance and uses of nitrifying bacteria and sulphur bacteria: on the examination of soils for potential bacteria-induced corrosive properties, the testing of gland packings, washers and other water-works materials and the examination of water for taint-producing micro-fungi and actinomycetes. Not everyone will agree with Dr. Windle Taylor's interpretation of the apparent speed with which nitrifying bacteria oxidise ammonia on rapid gravity filters, but the adequacy of the chapter for its intended purpose is beyond dispute. It forms a valuable addition to the text.

The important chapter on water-borne diseases has been enlarged and brought up to date, and it now includes a section on the menace to foodstuffs from contamination with polluted water and sewage sludge. The section devoted to physical and chemical analysis of water describes methods that have been developed during the last 10 years, and extensive use has been made of the publications of the Institute of Water Engineers and the American Public Health Association. Some older methods have been omitted, but many analysts will think that the process might have been carried further. It seems unnecessary, for example, to include in full working detail two obsolete methods for determining hardness in addition to describing the use of EDTA. These methods are already well known to older practitioners and are better disregarded by the young.

The original designers set the foundation of their work on the solid rock of basic principles. The value of each new storey lies in its ability to house the expanding knowledge of successive generations in harmony with the whole structure. Dr. Windle Taylor is unreservedly congratulated on the skill and expertise he has brought to the task of selecting and condensing all relevant advances of the past decade.

No doubt there will be many more editions: with so much to praise and admire in this one, suggestions are offered only in a constructive and deferential spirit. Valuable space could be made available for newer information by omitting working directions for analyses that are now fully described in authoritative specialist publications. Methods of investigating suspected pollution of surface waters by pesticides and herbicides are not yet far advanced, but the subject would seem to merit more extensive reference and documentation. The brief mention of plastic piping might have included a useful warning of the contamination that may occur from inward diffusion of coal gas and industrial vapours; the omission of any reference to methods by which residual silver was determined in water sterilised by the "Katadyn" process seriously detracts from the value of the recorded experience. Ever increasing demands on underground water supplies would justify more detailed guidance on the recognition of sea-water infiltration, and some reference might have been made to the absorption of residual synthetic detergents by activated carbon. Finally, the book has so much well merited authority that additional emphasis on the many dangers that may arise from complacent reliance on single-stage chlorination would not be out of place.

The cost of the new edition, alas, is £5; but in its pages the man with a problem may have access at will to accumulated knowledge and experience that is almost beyond price or praise. The consultant will continue to accept it as one of his best investments.

J. G. SHERRATT

ALIPHATIC FLUORINE COMPOUNDS. By A. M. LOVELACE, DOUGLAS A. RAUSCH and WILLIAM POSTELNEK. Pp. x + 370. *American Chemical Society Monograph No.* 138. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1958. Price $12.50; 100s.

Apart from some earlier work, particularly that of Swarts, the systematic study of organic fluorine compounds may be said to have begun about 1935. To-day, fluorine is a constituent of a wide range of commercial products, among others refrigerants, aerosol propellants, lubricants, rodenticides and insecticides, dyes, drugs and plastics.

The authors' aim has been to present a comprehensive account of the preparation and simpler physical properties of all classes of aliphatic (*i.e.*, acyclic and alicyclic) fluorine compounds. They do not claim that the Tables, extensive though they are, include every such compound that has been made. The literature has been combed up to 1955, with occasional later references.

The first chapter reviews general methods of fluorination, in particular the formation of the carbon - fluorine bond. The remaining twelve chapters deal with specific groups of compounds —alkanes, alkenes, alcohols, ethers, etc. After a short introduction, methods are described in general terms; details may be found from the references given for each compound listed. The index does not name individual chemicals, but it readily affords location; for example, fluoroacetamide is covered by the entry "amides" and can then be traced in the appropriate Table from its empirical formula. The reader should not be depressed by seeing that it may be made by method 1001; this merely means method 1 of chapter 10.

Attention is drawn to the fact that special techniques are often necessary for the satisfactory analysis of fluorocarbon compounds. B. A. ELLIS

Publications Received

BIOLOGICAL TREATMENT OF SEWAGE AND INDUSTRIAL WASTES. Edited by Brother JOSEPH McCABE, F.S.C., and W. W. ECKENFELDER, JUN. Volume II. Anaerobic Digestion and Solids-Liquid Separation. Pp. vi + 330. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1958. Price $10.00; 92s.

ESSENTIAL FATTY ACIDS. Edited by H. M. SINCLAIR. Pp. xviii + 268. London: Butterworths Scientific Publications; New York: Academic Press Inc. 1958. Price 50s.; $9.50.

EXPERIMENTAL DESIGNS IN INDUSTRY. Edited by VICTOR CHEW. Pp. xii + 268. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1958. Price $6.00; 48s.

RADIOAKTIVE ISOTOPE IN DER BIOCHEMIE. By ENGELBERT BRODA. Pp. viii + 326. Vienna: Verlag Franz Deuticke. 1958. Price Austrian S294.

GAS CHROMATOGRAPHY. Edited by VINCENT J. COATES, HENRY J. NOEBELS and IRVING S. FAGERSON. Pp. xii + 323. New York and London: Academic Press Inc. 1958. Price $12.00; 86s.

CHROMATOGRAPHISCHE METHODEN IN DER ANALYTISCHEN UND PREPARATIVEN ANORGANISCHEN CHEMIE UNTER BESONDERER BERUCKSICHTIGUNG DER IONENAUSTAUSCHER. By Priv.-Doz. Dr. Ing. EWALD BLASIUS. Pp. xx + 370. Stuttgart: Ferdinand Enke Verlag. 1958. Price (paper) DM96: (cloth boards) DM99.

No. 46 *of series Die chemische Analyse edited by Prof. Dr. Gerhart Jander.*

PRACTICAL CLINICAL BIOCHEMISTRY. By HAROLD VARLEY, M.Sc., F.R.I.C. Second Edition. Pp. viii + 635. London: William Heinemann Medical Books Ltd. 1958. Price 42s.

BRITISH NATIONAL FORMULARY 1957: First Amendment 1958. Pp. 11. London: The British Medical Association and The Pharmaceutical Press. 1958. Price 8d.

BRITISH PHARMACOPEIA 1958: Amendments, August, 1958. Pp. 5. London: The Pharmaceutical Press *for* The General Medical Council. 1958. Gratis.

*Copies of this leaflet may be obtained on application, enclosing a stamped addressed envelope, from The Secretary, British Pharmacopoeia Commission, General Medical Council Office, 44 Hallam Street, London, W.*1.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1957. Volume LIV. Pp. 445. London: The Chemical Society. 1958. Price 40s.

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CHESTER BEATTY RESEARCH INSTITUTE, Institute of Cancer Research: Royal Cancer Hospital. TECHNICIAN required for Physical Chemistry Laboratory. The work is particularly concerned with spectroscopic techniques and experience in the field or in electronics would be an advantage. The post is permanent and superannuable; salary according to qualifications and experience, applications, with the names of two referees, marked "E.R." should be addressed to the Secretary, Chester Beatty Research Institute, Fulham Road, London, S.W.3.

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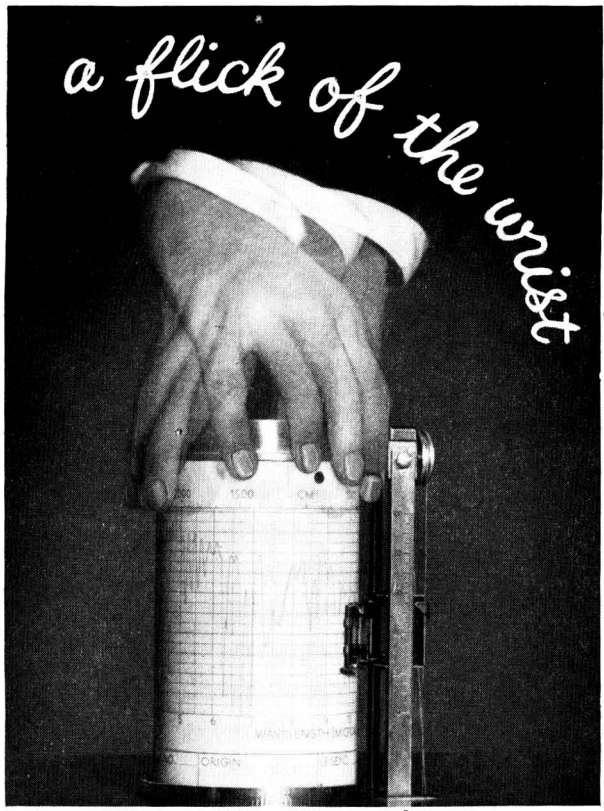

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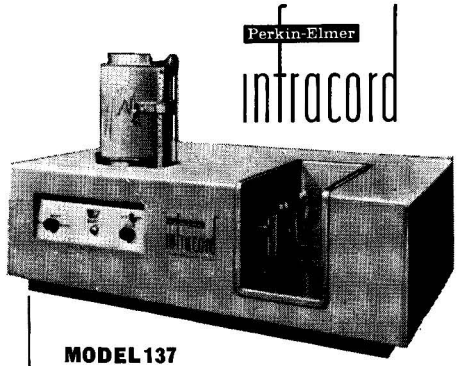

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