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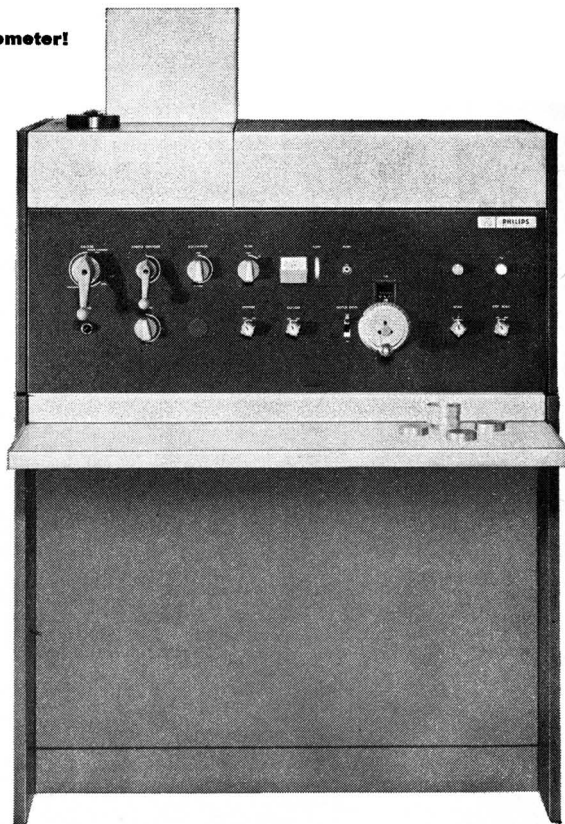
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Studies on the Analytical Chemistry of Hafnium and Zirconium

Part I. A Review of Methods for the Determination of Hafnium and Zirconium in Admixture

The available chemical and physical methods are discussed. The former are restricted to the determination of more than 0.1 per cent. of hafnium in zirconium. Emission spectrography, X-ray fluorescence and, especially, neutron-activation analysis can be used for trace hafnium determination in zirconium.

A. BROOKES and A. TOWNSHEND

Chemistry Department, The University, P.O. Box 363, Birmingham 15.

Analyst, 1970, **95**, 529-534.

Automatic Titration by Stepwise Addition of Equal Volumes of Titrant

Part I. Basic Principles

A method of titration has been developed, in which titrations are carried out by adding titrant stepwise in equal volumes to the sample, with measurement of potential after each addition. This method is well suited for automatic titrations, for example, in biochemical and process control analysis.

AXEL JOHANSSON

Royal Institute of Technology, Stockholm, Sweden.

Analyst, 1970, **95**, 535-540.

The Titrimetric Determination of Alumina in Ceramic Materials by Using DCTA in place of EDTA

The replacement of EDTA by DCTA (1,2-diaminocyclohexanetetraacetic acid) has a number of advantages. The reagent can be applied to the analysis of the silica - alumina range of materials and appears to be applicable to magnesites and chrome-bearing materials. The use of the reagent saves the time spent in boiling and cooling the solution so as to ensure that the alumina is fully complexed. As chromium does not react in the cold and aluminium does, the analysis of magnesites, dolomites and chrome-bearing materials would also be simplified. The method is described in detail.

H. BENNETT and R. A. REED

The British Ceramic Research Association, Queens Road, Penkhull, Stoke-on-Trent.

Analyst, 1970, **95**, 541-547.

Potentiometric Titration of Naphthyl Esters of Carboxylic Acids in Non-aqueous Solvent

A simple and rapid potentiometric method for the non-aqueous titration of naphthyl esters of carboxylic acids is described. This method enables free acid and ester in a sample to be distinguished in a single titration. The titration is performed with sodium methoxide in pyridine solution, the equivalence point being indicated by means of antimony and calomel electrodes with a potentiometer. In the first stage of the titration, the free acid present in an ester sample is neutralised, while in the second the ester is saponified by the titrant. If an ester contains only traces of free acid, determination of the latter on a separate, larger amount of sample is preferred.

A. GROAGOVÁ and V. CHROMÝ

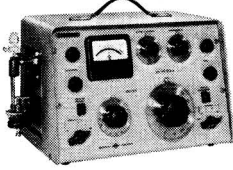
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Analyst, 1970, **95**, 548-551.

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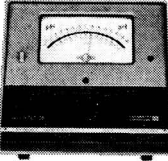
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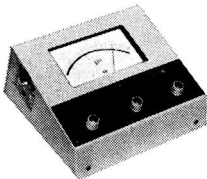
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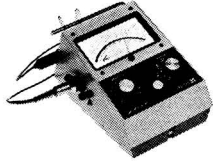
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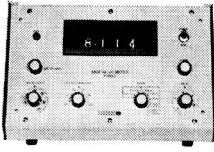
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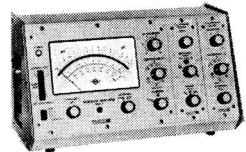
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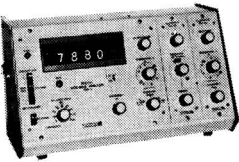
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Potentiometric Titration of Some Naphthyl Hydrogen Sulphates and Naphthyl Dihydrogen Phosphates

A rapid potentiometric titration of acid esters of naphthyl phosphates and sulphates based on acid-base properties of individual esters and their salts is described, and the values for their dissociation constants have been determined. Naphthyl dihydrogen phosphates and naphthyl hydrogen sulphates behave generally as di- and monobasic substances. Use of the proposed method, if combined with the determination of free naphthol and inorganic phosphates or sulphates, enables detailed analysis of such esters to be carried out.

V. CHROMÝ and A. GROAGOVÁ

Research Institute of Pure Chemicals, Lachema N.C., Brno, Czechoslovakia.

Analyst, 1970, **95**, 552-555.

Spectrophotometric Determination of Yttrium in Chromium and Chromium-base Alloys with Arsenazo III

A method has been developed for determining yttrium in the range 50 p.p.m. to about 4 per cent. in chromium and chromium-base alloys. The procedure involves the separation of yttrium from chromium(VI) by precipitation of yttrium hydroxide from an ammoniacal chloride solution; aluminium hydroxide is used as a "collector." The mixed hydroxides are dissolved in dilute nitric acid, and yttrium is subsequently determined spectrophotometrically by a procedure based on the formation of a blue-coloured complex with arsenazo III. Absorbance of the complex is measured at a wavelength of 660 nm.

The effects of common alloying constituents and likely impurities have been investigated, and modifications to the method have been introduced to overcome interference by aluminium, iron, titanium, zirconium, hafnium, niobium and tantalum.

D. F. WOOD and M. R. ADAMS

Imperial Metal Industries Limited, Kynoch Works, Witton, Birmingham 6.

Analyst, 1970, **95**, 556-561.

Electronic Modulation of Electrodeless Discharge Tubes for Use in Atomic Spectroscopy

A system for effecting modulation of the light output from microwave-excited discharge tubes by purely electronic means is described. The system is thought to have some advantages over the use of a mechanical chopper, and can be applied to instruments into which a chopper cannot be fitted.

P. C. WILDY and K. C. THOMPSON

Southern Analytical Limited, Frimley Road, Camberley, Surrey.

Analyst, 1970, **95**, 562-566.

The Interference of Cobalt, Nickel and Copper in the Determination of Iron by Atomic-absorption Spectrophotometry in an Air - Acetylene Flame

An investigation of interferences in the determination of iron by atomic-absorption spectrophotometry in an air-acetylene flame is reported. It has been found that three elements, cobalt, nickel and copper, exhibit serious depressive effects, the magnitude of which is strongly dependent on the flame conditions, with respect to both fuel-to-air ratio and the height of the optical path above the burner, and is also dependent on the anion present in the sample solution. The optimisation of the flame for both pure iron solutions and those containing the interfering elements, and means of suppressing these interferences, are discussed. The use of 8-hydroxyquinoline at a concentration equal to or greater than the total concentration of cobalt, nickel and copper is recommended as an effective releasing agent.

J. M. OTTAWAY, D. T. COKER, W. B. ROWSTON and D. R. BHATTARAI
Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow, C.1.

Analyst, 1970, **95**, 567-573.



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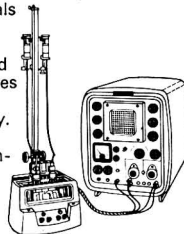
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Studies on the Analytical Chemistry of Hafnium and Zirconium

Part I. A Review of Methods for the Determination of Hafnium and Zirconium in Admixture

BY A. BROOKES AND A. TOWNSHEND

(Chemistry Department, The University, P.O. Box 363, Birmingham 15)

The available chemical and physical methods are discussed. The former are restricted to the determination of more than 0.1 per cent. of hafnium in zirconium. Emission spectrography, X-ray fluorescence and, especially, neutron-activation analysis can be used for trace hafnium determination in zirconium.

THE chemical properties of hafnium and zirconium are almost identical. The similarity is greater than for any other pair of elements, mainly because of their similar ionic radii ($\text{Hf}^{4+} = 0.78 \text{ \AA}$, $\text{Zr}^{4+} = 0.79 \text{ \AA}$) and outer electronic structure. It was not until a physical method of analysis (X-ray emission) was applied that the existence of hafnium was confirmed in 1922, although zirconium had been discovered in 1789.

Hafnium and zirconium can readily be determined in the presence of other elements, and can easily be separated from them. The analytical chemistry of the two metals has recently been reviewed.^{1,2} Their chemical similarity, however, makes the determination of hafnium in the presence of zirconium, and *vice versa*, a difficult but challenging analytical problem. Zirconium is used extensively for cladding enriched fuel rods in nuclear power plants because of its low thermal-neutron capture cross-section and its resistance to corrosion by superheated steam. Hafnium, however, has a much larger capture cross-section and its presence in zirconium is undesirable. It is essential, therefore, to have reliable methods for the determination of small amounts of hafnium in zirconium.

No chemical method is known in which only one of the metals responds, so that all available methods rely on one of the following differences between the two metals

- (1) differences in physical properties;
- (2) quantitative differences in chemical properties; and
- (3) differences in electronic and nuclear properties.

METHODS DEPENDING ON A PHYSICAL DIFFERENCE BETWEEN HAFNIUM AND ZIRCONIUM

As the two elements have the same ionic size but different atomic weights, the densities of the metals, and also of their compounds, differ. Thus, provided that the densities of the pure hafnium and zirconium compounds are known, the density of a compound containing a mixture of hafnium and zirconium can be used to determine the hafnium-to-zirconium ratio. de Hevesy³ reported that the densities of the mixed oxides and the densities of a mixture of $(\text{NH}_4)_2\text{HfF}_6$ and $(\text{NH}_4)_2\text{ZrF}_6$ could be used.

He also determined³ the hafnium-to-zirconium ratio by determining the ammonia content of the mixture of compounds $(\text{NH}_4)_2\text{HfF}_6$ and $(\text{NH}_4)_2\text{ZrF}_6$. The percentages by weight of ammonia in the pure compounds are different, and so the percentage by weight of the ammonia in a mixture of the compounds is a measure of the hafnium-to-zirconium ratio. de Hevesy used the halide analysis of the mixed chlorides or bromides in the same way.

If hafnium and zirconium can be precipitated together to give a mixture of stoichiometric compounds suitable for direct weighing, and if, after weighing, the precipitates can be converted into another stoichiometric, weighable compound, then, from the results obtained it is possible to calculate the hafnium-to-zirconium ratio. This principle was used by Claassen,⁴ who used the selenites as his first weighable precipitate and the oxides as the second. To obtain the stoichiometric selenites it was necessary to heat the precipitate in its liquor for up to 20 hours before filtering, and so the analysis was very time consuming.

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The same principle was used by Fujiwara,^{5,6} who used the pyrophosphates and the oxides as the weighing forms. The interconversion of these compounds is difficult and time consuming. Hahn⁷ used the *p*-bromomandelates and oxides as weighing forms. Strict control of the conditions was necessary to obtain the stoichiometric *p*-bromomandelate precipitate, but this could be converted into the oxide simply by heating. The method was found to be inaccurate when the amount of hafnium in zirconium was below 10 per cent.

Freund and Holbrook⁸ devised a differential spectrophotometric method for the determination of zirconium in the presence of hafnium. They found that the two elements reacted with alizarin red S in an identical manner and that the molar extinction coefficients were the same. Starting with a constant weight of mixed oxides, the number of moles of metals, and hence the absorbance of the solution containing the metals, decreased as the proportion of hafnium oxide by weight in the constant weight of mixed oxides increased. A normal spectrophotometric method would involve the use of such small amounts of oxides that the variations in absorbance would be small. The differential method required larger amounts of oxides and hence gave greater variations in absorbance.

According to Bachman and Banks,⁹ Johnson¹⁰ studied mandelic acid, quercetin and xylenol orange as possible reagents for the differential spectrophotometric determination of hafnium in zirconium, and found xylenol orange to be the most satisfactory. Johnson and Freund¹¹ later produced a differential method in which chloranilic acid in 2 M acid was used. Mel'chakova, Trubetskaya and Peshkova¹² used arsenazo III to determine zirconium in the presence of hafnium by using the same basic principles. Crepaz, Marchesini and Mazzolini¹³ used a large constant weight of mixed oxides in the same way as in the other methods, but found that better accuracy could be obtained by measuring different variables of the system.

METHODS DEPENDING ON A CHEMICAL DIFFERENCE BETWEEN HAFNIUM AND ZIRCONIUM

In 1926, de Boer¹⁴ reported a difference between hafnium and zirconium in their reactions with rufigallic acid, but this was not used analytically. de Boer and Emmens¹⁵ reported that in an alkaline solution the optical rotation of tartaric acid was increased in the presence of zirconium. This increase was less marked for hafnium. This difference was used as the basis of an analytical method for the determination of zirconium-to-hafnium ratios by Wernimont and de Vries.¹⁶

Mayer and Bradshaw¹⁷ stated that the molar extinction of the hafnium - alizarin red S lake was almost exactly one quarter of the molar extinction of the zirconium - alizarin red S lake. They used a constant number of moles of hafnium *plus* zirconium and found that the absorbance obtained was related to the molar hafnium-to-zirconium ratio. The method was used to grade roughly zirconium - hafnium alloys.

Kuznetsov and Nemodruk¹⁸ reported that the complexes of the metals with 2,4-disulphobenzenaurin-3',1''-dicarboxylic acid had different stabilities. By measuring the absorbance at low acidities they determined the total amount of the metals present. They then measured the absorbance at a higher acidity, which largely destroyed the hafnium complex, to obtain the amount of zirconium present. The amount of hafnium present was found by difference.

Kononenko, Lauer and Poluektov¹⁹ utilised the differing stabilities of the metal complexes with arsenazo I. When the acidity was increased from 0.25 N hydrochloric acid to 1.0 N hydrochloric acid, the optical density decreased by a factor of 2 for zirconium and 19 for hafnium. They took a fixed weight of oxides and obtained a calibration graph by plotting the ratio of optical densities measured at the two acidities against the percentage by weight of hafnium oxide in the sample. They determined 20 to 100 per cent. w/w of hafnium oxide.

Elinson and Mirzoyan²⁰ used the differing stabilities of the metal complexes with arsenazo III as the basis for the determination of zirconium in hafnium. They used a constant acidity of 4 N hydrochloric acid and a constant total weight of hafnium *plus* zirconium, and were able to determine zirconium in the range 0 to 20 per cent. w/w in hafnium.

Cheng^{21,22,23} produced a series of papers on the reactions of xylenol orange with the metals. He found that the hafnium complex was less stable than the zirconium complex, but did not produce a quantitative method based on this observation. He also reported that hydrogen peroxide completely prevents the formation of a zirconium complex, but only decreases the amount of hafnium complex formed. When analysing mixtures of hafnium and zirconium he found that the presence of zirconium in amounts comparable with those of hafnium lowered the absorbance due to hafnium. By adding sulphate ions he was able to

decrease this effect. His results suggest that 0 to 0.5 μ mole of hafnium can be determined with no interference from 0.5 μ mole of zirconium. If the relative amount of zirconium is increased above this level, the absorbance due to the hafnium complex is again reduced.

Hydrogen peroxide was also used by Cerrai and Testa²⁴ in their work on the metal complexes of quercetin. They reported that adding hydrogen peroxide lowered the absorbance due to the zirconium complex while the absorbance due to the hafnium complex was only slightly reduced. They found that by using a constant total number of moles of hafnium plus zirconium the absorbance increased as the relative amount of hafnium increased. The lowest working range for this method was 0 to 5 per cent. moles of hafnium.

Yagodin, Chekmarev and Vladimirova²⁵ made a study of the metals in sulphuric acid, and found that in 2 N sulphuric acid, zirconium ions give an absorption maximum at 200 to 220 nm, whereas hafnium solutions show no absorption. Thus the zirconium content was determined directly and the hafnium content found by difference. Horiuchi and Nishida²⁶ studied the complexes of the metals with chrome azurol S and described methods for the simultaneous determination of hafnium and zirconium based on the fact that hydrogen peroxide decolorised the complexes at different rates.

A catalytic method for the simultaneous determination of each metal was described by Yatsimirskii and Raizman.²⁷ They found that both metals catalysed the reaction of iodide ions with hydrogen peroxide, but that the metals reached their maximal catalytic activity at different pH values. By following the reaction at these two pH values, they were able to determine both zirconium and hafnium in admixture. They did not attempt to determine less than 0.6 μ mole of hafnium in 12 μ mole of zirconium.

Challis²⁸ has described a method for the simultaneous determination of the two metals with xylenol orange. By measuring the absorbances at three different acidities, which were chosen such that both the hafnium and zirconium complexes were in various degrees of dissociation, the amounts of both hafnium and zirconium could be determined. He did not attempt to determine less than 10 μ g of hafnium in the presence of 50 μ g of zirconium.

METHODS DEPENDING ON AN ELECTRONIC OR NUCLEAR DIFFERENCE BETWEEN HAFNIUM AND ZIRCONIUM

These methods depend on the techniques of X-ray spectrography, emission spectrography and nuclear-activation analysis. Many methods involving these techniques have been published, so no attempt will be made to present a complete survey. Instead, the factors involved in applying the techniques to the determination of the metals are presented, together with the publications marking major developments in the determination of hafnium in zirconium.

METHODS INVOLVING X-RAY SPECTROGRAPHY—

One of the most striking successes of X-ray spectrography as an analytical tool was its use in the discovery of hafnium. However, its application as a quantitative analytical technique had a serious drawback. Because of the high excitation potential of the lines of the K-series of the X-ray spectrum of hafnium, it is only practical to use the lines of the L-series for the determination of hafnium. However, the $K\alpha_1$ and $K\alpha_2$ lines of the X-ray spectrum of zirconium in the second order of reflection overlap the most sensitive lines ($L\alpha_1$ and $L\alpha_2$) of the spectrum of hafnium in the first order of reflection. Thus measuring the intensity of the hafnium lines was very difficult.

The first methods in which X-ray spectrography was used involved incorporating the sample as the anode in an X-ray tube. This is a time-consuming process and for this reason X-ray fluorescence spectrography, in which the sample is irradiated with X-rays, is preferred.

de Hevesy³ used the former method and used the $L\beta_1$ line of hafnium to determine the element. As this is a weaker line, some sensitivity and precision were lost. The most sensitive lines of hafnium have a lower excitation potential than the zirconium lines that overlap them. Vainshtein, Shevaleevskii and Shtauberg²⁹ found that by selecting an operating voltage for the X-ray tube near to or equal to the excitation potential of the zirconium line, the intensity of the interfering zirconium lines could be appreciably diminished. Lowering the voltage lowered the sensitivity towards the hafnium line, the sensitivity being 0.2 per cent. of hafnium in zirconium.

Birks and Brooks³⁰ used X-ray fluorescence spectrography. By using a 16-inch long collimator they were able to resolve the hafnium $L\beta_2$ line, thus directly determining the hafnium; but the long collimation led to a lower counting rate, which reduced the accuracy. They obtained better accuracy by plotting the ratio of the peak intensities of the hafnium $L\beta_2$ line to the unresolved hafnium $L\beta_1$ line plus second order zirconium $K\beta$ doublet against increasing amounts of hafnium. The sensitivity was about 0.1 per cent. of hafnium in zirconium. They also reduced the X-ray tube voltage to reduce the intensity of the zirconium lines but again found that the precision decreased.

Mortimore and Romans³¹ used a 16-inch collimator to resolve the hafnium $L\beta_1$ first-order line from the zirconium $K\beta_1$ second-order line, but found that zirconium interfered if the absolute intensity of the hafnium line was used. They found that the best accuracy was obtained by plotting the log of the ratio of the intensities of the two lines mentioned against the log of the concentrations. They determined hafnium in the range 0.1 to 40 per cent. in zirconium.

Despujols and Lumbroso³² utilised the $L\beta_2$ line of hafnium. They used a curved aluminium crystal as the diffracting crystal, among other refinements, to increase the precision. The reported sensitivity of the method is 0.016 per cent. of hafnium in zirconium, but the counting time was a few hours if trace amounts of hafnium were to be determined. Bermudez Polonio³³ used the hafnium $L\alpha_1$ line. His analysing crystal was of germanium, cut so as to block the second-order zirconium $K\alpha$ radiation. He reported a limit of detection of 150 p.p.m. of hafnium oxide in zirconium oxide, although this could probably be improved by one order of magnitude with the use of current instrumentation. Ramous³⁴ reported that between 100 and 200 p.p.m. of hafnium in zirconium could be determined with an error of 45 p.p.m. by using an X-ray tube with the voltage lowered to eliminate the fluorescence due to zirconium $K\alpha_1$ radiation. Thus he was also able to use the most sensitive hafnium line.

METHODS INVOLVING EMISSION SPECTROGRAPHY—

Like the X-ray spectrography of hafnium and zirconium, their emission spectrography is not complicated by their chemical similarity. This similarity is in some ways an advantage because it enables zirconium to be used as an internal standard in the determination of hafnium. However, their emission spectrography is complicated by their refractory nature, that is, they are extremely difficult to volatilise. Thus the major difficulty in the spectrographic determination of the elements is to secure uniform and reproducible volatilisation. Once this has been achieved the determination of the elements is straightforward.

The method of excitation chosen depends on the physical characteristics of the sample; direct and alternating arc excitations are often used when the sample is in powder form, whereas spark excitation is usually used for alloys and samples in solution.

Morgan and Auer³⁵ described an early application of the technique in their semi-quantitative determination of hafnium and other elements in zircons. Feldman³⁶ used a porous cup electrode and spark excitation in his determination of hafnium in zirconium solutions, the range being 0.7 to 9.3 per cent. of hafnium in zirconium. Fassel and Anderson³⁷ mixed the sample with graphite to form a conducting briquet, which they excited with over-damped condenser discharges from a "multisource" type excitation unit. By choosing several different spectral lines they determined hafnium in zirconium in many ranges, the lowest being 0.1 to 6.4 per cent. of hafnium in zirconium.

Kingsbury and Temple³⁸ used an impulse arc as an excitation source and determined 0.01 to 55 per cent. of hafnium in zirconium. Mortimore and Noble³⁹ mixed the powdered oxide with barium fluoride and graphite so as to achieve a steady volatilisation. They were able to determine 0.003 to 1.0 per cent. of hafnium in zirconium. Solodovnik and Kondrashina⁴⁰ reported that the barium fluoride was unnecessary, and achieved the same sensitivity with a high dispersion grating spectrograph.

Gavrilov, Fedorovskaya and Yakhimovich⁴¹ stated that the powerful electric arcs used in the previous methods produced spectral lines from carbon and from impurities in the samples. These prevented the use of one hafnium spectral line, which has a high intensity. Accordingly, they used a less powerful arc and reported a sensitivity of 4×10^{-4} per cent. of hafnium in zirconium. However, Solodovnik and Kondrashina⁴⁰ used this line as did Elwell and Wood,⁴² the latter reporting a sensitivity of 0.003 per cent. of hafnium in zirconium.

THERMAL-NEUTRON ACTIVATION ANALYSIS—

As the hafnium nucleus has a much larger activation cross-section than zirconium, it can be more conveniently determined by the activation method. The technique is especially suited for the determination of hafnium in the presence of zirconium.

The technique has been applied in two distinct ways. The first involves a short irradiation of the sample followed by immediate counting of the short-lived isotope, hafnium-179m ($t_{1/2} = 19$ s), that is produced. This involves counting at the reactor site. The second involves irradiating the sample for several days and then counting the hafnium-175 and hafnium-181 that are produced. As these isotopes have relatively long half-lives (46 days and 70 days, respectively) counting can be delayed, thus enabling the determination to be carried out away from the reactor.

As early as 1943, Aten⁴³ used the first approach to determine 10 per cent. of hafnium in zirconium. He had only a small neutron flux at his disposal. The same was true for Stribel,⁴⁴ but with more sensitive counting equipment he determined amounts as low as 100 p.p.m. of hafnium in zirconium. Mackintosh and Jarvis⁴⁵ used a larger neutron flux and estimated their limit of detection as 7 p.p.m. of hafnium in zirconium. Their zirconium samples were not pure enough for them to verify this figure experimentally.

Mignonsin and Albert⁴⁶ determined twenty-two elements, including hafnium, in zirconium metal prepared from the Van Arkel and Kroll processes. In their determination of hafnium they first separated the hafnium from the zirconium by ion exchange and then irradiated it. Their estimated sensitivity was 0.01 p.p.m. of hafnium in zirconium, with an error of 3 p.p.m. at the 60 p.p.m. level. Haerdi, Balsenc and Monnier⁴⁷ analysed zirconium metal without separation and reported a limit of detection of 1×10^{-3} p.p.m., their error being 15 per cent. at the 1.4 p.p.m. level. Their estimated absolute limit of detection of hafnium was 10 pg. The time for a single analysis was 15 minutes.

Mackintosh and Jarvis⁴⁵ also used the second method involving the longer-lived isotopes. However, in irradiating the samples for several days, many other activities were produced, derived from the zirconium, impurities and alloying constituents. They found it necessary to separate the hafnium by ion exchange before counting. The sensitivity was about 10 p.p.m. of hafnium in zirconium. Girardi, Guzzi and Pauly⁴⁸ used lithium-drifted germanium solid-state detectors. Although these have a lower sensitivity than scintillation counters, they can resolve γ -rays of different energies. Thus the interference caused by the other activities was eliminated and the hafnium determined without separation. After irradiation for 2 hours, the sample was left for 2 to 7 days to allow for the decay of the short-lived activities. Their limit of detection was 10 p.p.m. of hafnium in the zirconium.

FLAME SPECTROSCOPY—

The detection limits for the determination of zirconium and hafnium by their emission in an oxy-acetylene pre-mixed flame are 50 and 75 p.p.m., respectively,⁴⁹ whereas those for atomic absorption in the same flame are 5 and 15 p.p.m., respectively.⁴⁹ These limits are improved to 0.01 and 0.005 p.p.m. when emission from an induction-coupled plasma is measured.⁵⁰ However, no reports of the application of these techniques to the analysis of mixtures of zirconium and hafnium have been reported.

MASS SPECTROMETRY—

Jackson and Whitehead⁵¹ reported limits of detection of 0.2 and 4 p.p.m. for zirconium and hafnium, respectively, when determined in a titanium dioxide matrix by spark-source mass spectrometry. Recently, hafnium and zirconium (and titanium) have been determined in admixture by formation of their volatile chelates with benzoyltrifluoroacetylacetone and utilisation of the integrated ion current technique. The absolute limits of detection were 10^{-14} g of zirconium and 10^{-12} g of hafnium.⁵²

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Automatic Titration by Stepwise Addition of Equal Volumes of Titrant

Part I. Basic Principles

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A method of titration has been developed, in which titrations are carried out by adding titrant stepwise in equal volumes to the sample, with measurement of potential after each addition. This method is well suited for automatic titrations, for example, in biochemical and process control analysis.

THE automatic potentiometric titrators commercially available fall into two main classes: those in which a complete titration curve is plotted, and those in which the addition of the titrant is stopped at the equivalence point.

In the first type of instrument the titrant is added continuously to the sample solution, and the variation in potential is simultaneously recorded. The equivalence point is read directly from the resulting graph and the titrant must be delivered slowly, particularly near this point, to permit equilibrium to be reached.

Instruments of the second type discontinue addition of titrant when a pre-set potential difference has been reached, and the equivalence volume is read from the burette. Reagent flow is rapid at the beginning of the titration but it must be reduced as the pre-set potential is approached.

In both instances one titration takes about 10 minutes.

This is the first of a series of papers describing a third method of titration which is particularly suitable for computerised data handling, and which gives good results for some titrations that are unsatisfactory by the above two methods. The method is of general applicability, although so far it has only been used for the titration of acids with strong bases and could be used, for example, for complexometric titrations.

The titration is carried out by transferring a known volume of sample to a container and measuring the pH. The base is then added stepwise in equal volumes and the pH measured after each addition.

Obviously, the volume of base equivalent to the acid cannot be directly measured: the equivalence point must be calculated. This is a disadvantage, but in many instances the method has important compensating advantages.

(i) Titrations can be carried out more rapidly, as it is only necessary to wait for equilibrium at a few stages in the titration. This is particularly significant with precipitation and complexometric titrations, where equilibrium is reached slowly.

(ii) Titrations can be carried out more accurately, as several values are used for calculation of the equivalence volume. This is of special importance when a mixture of strong and weak acids is titrated. If, for example, a mixture of 95 per cent. hydrochloric acid and 5 per cent. acetic acid is titrated, there is only one break in the pH - volume curve. By using values before the equivalence point, when only the strong acid is titrated, and values after the equivalence point, when both acids have been titrated, good results can be obtained. The values near the equivalence points are not as useful, as both acids contribute to the measured pH value (see Fig. 4).

(iii) The method also permits the use of values obtained after the equivalence point which may be advantageous, *e.g.*, for precipitation titrations, when precipitation is complete and equilibrium is rapidly reached.

(iv) The method is well suited for automatic titration. A titrator has been constructed for the repetitive analysis of similar samples, which has a capacity for 200 samples and an analysis rate of 30 titrations per hour. This apparatus will be described in Part II. At

this rate of analysis computerised data handling is desirable, and the titration principle described is well suited for such calculations.

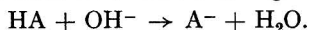
This paper gives formulae for the calculation of equivalence volumes from a set of pH - titrant volume data.

CALCULATION OF EQUIVALENCE VOLUME—

In theory, if only one acid is present and its dissociation constant is known, there is no need to carry out a titration; the concentration can be calculated directly from the pH of the acidic solution. In practice this will not give sufficient accuracy and at least two pH - titrant volume values are required. If more than two values are available, they can be used to calculate the equivalence point with increased precision. The simplest and most precise method of using all the experimental values available is to convert the titration curve into a straight line. For example, in the titration of a strong acid with a strong base, the hydrogen-ion concentration decreases linearly with addition of base until the equivalence point is reached.

Thus if the hydrogen ion concentration $[H^+] = 10^{-pH}$ is plotted against volume of base added, a straight line is obtained that intersects the volume axis at the equivalence volume.

For the titration of a weak acid, HA, with a strong base, the main reaction is



Thus the concentration of acid decreases and the concentration of A^- increases linearly with addition of base. At the equivalence point the concentration of free acid is low. In this case $[HA]$, which has been calculated from experimental results, is plotted against volume of base added. The equilibrium equation is as follows—

$$[HA] = K[H^+][A^-]$$

where K is the stability constant of the acid, $[H^+]$ is equal to 10^{-pH} and $[A^-]$ is proportional to the volume, V , of base added. If, therefore, $10^{-pH} \times V$ is plotted against V , a straight line is obtained which intersects the V -axis at the equivalence volume. In both instances the hydroxide ion concentration increases linearly with addition of base after the equivalence point.

This method of calculation was first described by Sørensen¹ and investigated in more detail and applied to more complex systems by Gran,² who plotted values of suitable functions which give straight lines with points of intersection at the equivalence points.

If the equation for such a straight line is given by—

$$ky + x = l$$

then Gran's expressions for x , y , k and l are summarised in Table I.

TABLE I
GRAN'S EXPRESSIONS FOR x , y , k and l

	x	y	k	
Weak acid before the equivalence point	V	$V \times 10^{-pH}$	$\frac{1}{K_a}$	V_e
Strong acid before the equivalence point	V	$(V_0 + V)10^{a-pH}$	1	V_e
Strong or weak acid after the equivalence point ..	V	$(V_0 + V)10^{pH-b}$	1	V_e

V = volume of titrant added, V_0 = volume of sample solution before titration, V_e = volume of titrant added at the equivalence point, K_a = dissociation constant of the acid, and a and b are suitably chosen constants.

Thus the points (x_1, y_1) , (x_2, y_2) . . . (x_n, y_n) are plotted, where x is base added, ml, y is the expression above, calculated from pH values, and n is the number of measurements. A straight line is drawn through the points (x_1, y_1) and its intersection with the x -axis gives the volume of titrant, V_e , at the equivalence point. This line of best fit is usually estimated visually, although it is better to use the method of least squares. The functions given by Gran do not, however, give perfectly straight lines, *e.g.*, at the beginning of the titration of a weak acid. Although those points not on the straight line can be ignored with hand plotting, the problem can be avoided by deriving functions that give lower deviations from linearity.

TITRATION OF AN ACID WITH A STRONG BASE—

Consider the case where V_0 ml of an acid of concentration C_A is titrated with V ml of a strong base, e.g., sodium hydroxide, of concentration C_B . The following relationships apply.

The stability constant ("mixed constant") of the acid HA is—

$$\frac{[HA]}{\{H\}[A]} = K \quad \dots \quad (1).$$

(For simplicity, ionic charges are omitted throughout the paper.) $\{H\}$ denotes activity of hydrogen ions.

The total concentration of acid, C_{HA} , after addition of V ml of base [total volume therefore being $(V + V_0)$ ml], is—

$$C_{HA} = [HA] + [A] = \frac{C_A V_0}{(V + V_0)} \quad \dots \quad (2).$$

At the equivalence point, after addition of V_e ml of base—

$$V_0 \times C_A = V_e \times C_B \text{ (by definition)} \quad \dots \quad (3).$$

Combination of equations (1), (2) and (3) gives—

$$[A] = \frac{V_e \times C_B}{(V_0 + V)(1 + K\{H\})} \quad \dots \quad (4).$$

The condition for electrical neutrality—

$$[H] + [Na] = [OH] + [A]$$

and the expression $[Na] = \frac{V}{(V_0 + V)} \times C_B$ are also included, yielding—

$$V_e - V = K(V\{H\} + \frac{V_0 + V}{C_B} \{H\} [H] - \frac{V_0 + V}{C_B} \{H\} [OH]) + \frac{V_0 + V}{C_B} ([H] - [OH]) \quad \dots \quad (5).$$

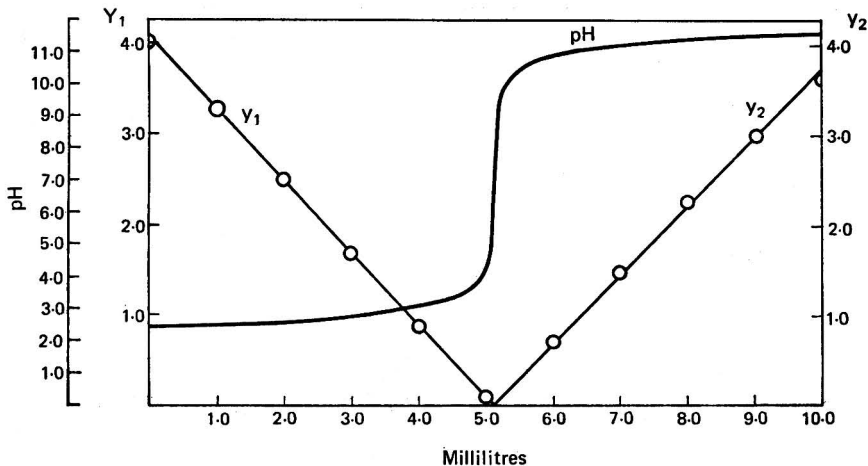


Fig. 1. Titration of 100.0 ml of 5.16×10^{-3} M hydrochloric acid with 0.0996 M sodium hydroxide solution. Both solutions were also 0.1 M with respect to potassium chloride. The pH - ml base curve was obtained with a Metrohm Potentiograph E336 recording titrator equipped with a 120 U glass electrode. The lines

$y_1 = (V_0 + V) \times 10^{-pH}/C_B$ and $y_2 = (V_0 + V) \times K_w/(C_B \times 10^{-pH})$ were calculated from pH - ml base data

STRONG ACIDS—

For strong acids, HA is not present in the solution. The proton complex constant is therefore 0, and the first term in equation (5) disappears. The remainder of the expression is identical with Gran's expression for the titration of a strong acid, provided [OH] before the equivalence point, and [H] after the equivalence point, are neglected.

Thus, before the equivalence point—

$$V_e - V = \frac{V_0 + V}{C_B} [H] \quad \dots \quad (6)$$

and after the equivalence point—

$$V_e - V = -K_w \frac{V_0 + V}{C_B} \cdot \frac{1}{[H]} \quad \dots \quad (7)$$

where K_w = ionic product of water.

Fig. 1 shows the titration of 100 ml of 5.16×10^{-3} M hydrochloric acid with 0.0996 M sodium hydroxide solution. The titration was performed with a recording titrator equipped with a glass electrode.

$$y_1 = \frac{V_0 + V}{C_B} \{H\} \text{ and } y_2 = -\frac{V_0 + V}{C_B} \cdot \frac{K_w}{\{H\}}$$

were calculated from the same experimental results and plotted against volume of base added. It is not necessary to convert activities into concentration. This will alter the gradient of the curves, but it will not affect the determination of the equivalence volume.

WEAK ACIDS—

For the titration of weak acids other terms in equation (5) can be neglected before the equivalence point. The remaining expression

$$V_e - V = K(V\{H\} + \frac{V_0 + V}{C_B} \{H\} [H]) \quad \dots \quad (8)$$

s that of the equation for a straight line—

$$l - x = ky$$

where x = volume of base added,

l = volume of base added at the equivalence point,

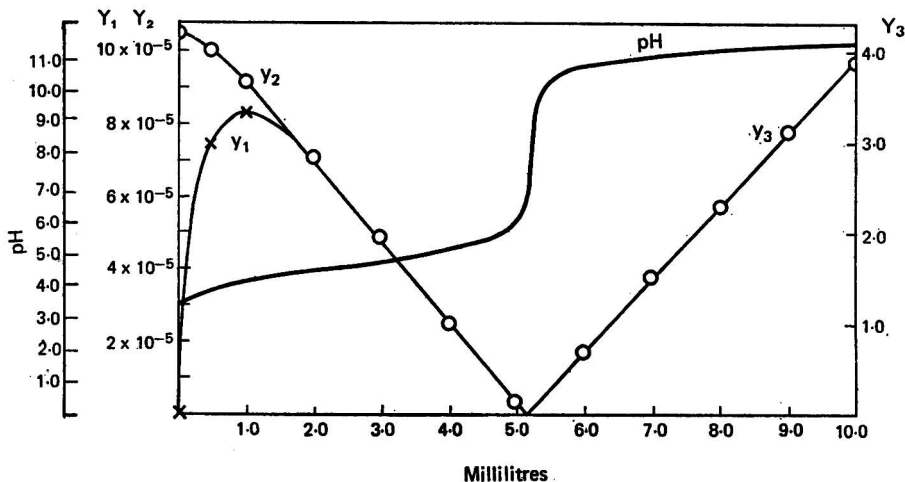


Fig. 2. Titration of 100.0 ml of 5.14×10^{-3} M acetic acid with 0.0996 M sodium hydroxide solution. Both solutions were also 0.1 M with respect to potassium chloride. The same equipment as for Fig. 1 was used

and $y_1 = V \times 10^{-pH}$ and $y_2 = V \times 10^{-pH} + (V_0 + V) \times 10^{-(pH + pCH)}/C_B$ and $y_3 = (V_0 + V) \times K_w / (C_B \times 10^{-pH})$ were calculated from the pH - ml base curve. pCH is $-\log[H] = pH - 0.08$

$$y = V\{H\} + \frac{V_0 + V}{C_B} \{H\} [H] \text{ and } \dots \dots \dots (9)$$

$k = K =$ stability constant of the acid.

Thus for given values of volume of base added, V , and of values of y , calculated from equation (9), the equivalence volume and the stability constant of the acid can be calculated.

Comparison of equation (8) with the corresponding Gran equation shows that Gran has disregarded the last term. This is a reasonable approximation, except when V is small.

After the equivalence point, when the hydrogen ion concentration is low, equation (5) is of the same form as for strong acids (equation 7).

Both equations (7) and (8) give straight lines, and values of dissociation constants are not required.

In Fig. 2, the results of a titration of acetic acid are given: 100 ml of 5.14×10^{-3} M acetic acid were titrated with 0.0996 M sodium hydroxide solution with the same equipment as in the titration shown in Fig. 1. Plots of $y_1 = V[H]$, $y_2 = V\{H\} + \frac{V_0 + V}{C_B} \{H\} [H]$ and

$$y_3 = \frac{V_0 + V}{C_B} \times \frac{K_w}{\{H\}}$$

The expression for y_2 does not give a straight line at the beginning of the titration, although the result is much better than for y_1 . This is because the term $\frac{V_0 + V}{C_B} [H]$ has been neglected. The effect of this term is greatest for relatively strong acids in dilute solution, although even in these cases results obtained after the equivalence point give correct equivalence volumes.

For the titration of very weak acids all terms in equation (5) must be considered. Ingman and Still³ have treated this problem graphically.

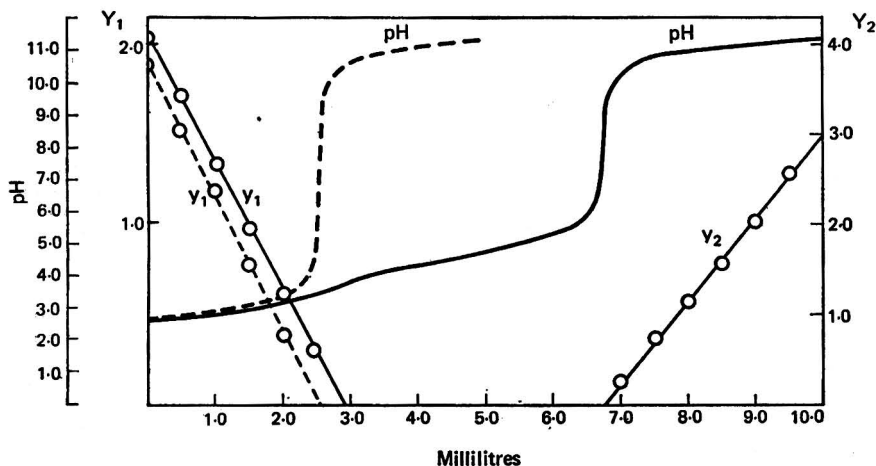


Fig. 3. Hydrochloric acid alone (dotted lines) and a mixture of hydrochloric acid and acetic acid (solid lines) were titrated as above. The curves $y_1 = (V_0 + V) \times 10^{-pH}/C_B$ for hydrochloric acid titrations and $y_2 = (V_0 + V) \times K_w/(C_B \times 10^{-pH})$ for the mixture of acids have been calculated from pH - ml base data. Theoretical values for equivalence volumes are 2.55 and 6.72 ml, respectively, as shown in the text

MIXTURES—

The titration of mixtures is more complicated. Fig. 3 shows the titration of hydrochloric acid alone (dotted lines), and of a mixture of hydrochloric acid and acetic acid (solid lines). The amount of hydrochloric acid is the same in both instances and is equivalent to 2.55 ml of standard hydroxide solution: total acid content corresponds to 6.72 ml of hydroxide

solution. The figure shows that the curves calculated from equations (6) and (7) give accurate equivalence volumes for the pure hydrochloric acid solution, and for total acid content only.

The equivalence volume for hydrochloric acid in the mixture, 2.90 ml, is too high as the curve cannot be extrapolated to $y = 0$ because of the partial dissociation of acetic acid into hydrogen ions. However, these preliminary values, 2.90 and 3.82 ml for hydrochloric acid and acetic acid, respectively, can be easily corrected. At this acetic acid concentration (3.82×10^{-3} M) the degree of dissociation, α , is about 8 per cent. [from $\log \alpha = -0.5 (\log C + \log K)$]. The equivalence volume of hydrochloric acid should therefore be reduced by 0.34 ml. This gives values of 2.56 and 4.16 ml for the strong and weak acids, respectively, compared with theoretical values of 2.55 and 4.17 ml.

The degree of dissociation varies with concentration. A 0.01 M solution of acetic acid is 4.5 per cent. dissociated, while a 0.001 M solution is 15 per cent. dissociated, and it is desirable to titrate solutions as concentrated as possible. The method gives good results for small amounts of acetic acid in relatively large amounts of hydrochloric acid, but small amounts of strong acid in large amounts of weak acid are difficult to determine.

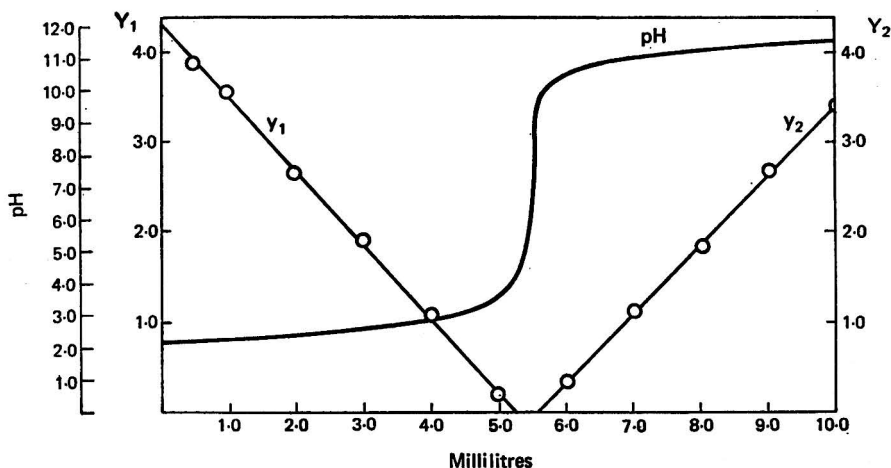


Fig. 4. A mixture of about 95 per cent. of hydrochloric acid and 5 per cent. of acetic acid was titrated as above. The usual pH - ml base curve shows only one asymmetric point of inflexion. The curves $y_1 = (V_0 + V) \times 10^{-\text{pH}}/C_B$ and $y_2 = (V_0 + V) \times K_w/(C_B \times 10^{-\text{pH}})$ give equivalence volumes of 5.30 and 5.55 ml, compared with theoretical values of 5.32 and 5.58 ml, respectively

A titration of a mixture of acetic acid and hydrochloric acid (1 + 19) is shown in Fig. 4.

The usual pH versus volume of base, ml, curve shows only one point of inflexion, while the above method yields correct values for the equivalence volumes: 5.30 and 5.55 for the strong and weak acids, respectively, compared with theoretical values of 5.32 and 5.58 ml.

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The Titrimetric Determination of Alumina in Ceramic Materials by Using DCTA in place of EDTA

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The replacement of EDTA by DCTA (1,2-diaminocyclohexanetetra-acetic acid) has a number of advantages. The reagent can be applied to the analysis of the silica - alumina range of materials and appears to be applicable to magnesites and chrome-bearing materials. The use of the reagent saves the time spent in boiling and cooling the solution so as to ensure that the alumina is fully complexed. As chromium does not react in the cold and aluminium does, the analysis of magnesites, dolomites and chrome-bearing materials would also be simplified. The method is described in detail.

THE British Standard method for the analysis of high-silica, aluminosilicate and aluminous^{1,2,3} materials includes the titrimetric method for the determination of alumina by using ethylenediaminetetra-acetic acid (EDTA). The same procedure is used in the amended versions, which utilise the coagulation technique⁴ for the determination of silica. In these methods an aliquot of the stock solution, obtained after the removal of the bulk of the silica by dehydration or coagulation, is used for the determination of alumina. The iron and titanium are removed by solvent extraction with cupferron and chloroform and, after adjusting the acidity, an excess of EDTA is added, followed by a buffer solution. The solution is boiled for 10 minutes to ensure that the alumina is completely complexed by the EDTA. It is then cooled and the back-titration of the excess of EDTA carried out by using zinc solution with dithizone as indicator in the presence of ethanol.⁵ The latter is present to ensure the solubility of the indicator.

The time taken to complete the determination from the moment of taking the aliquot is normally 75 to 90 minutes, of which only about 20 to 25 minutes are "analyst" time, the remainder being taken up with boiling and cooling the solution. It is known that the newer complexometric reagent, 1,2-diaminocyclohexanetetra-acetic acid (DCTA), will react completely with aluminium in the cold,⁶ and that it has been applied to the determination of alumina in silicate materials.^{7,8,9} Thus, if it is possible to use this reagent for this determination, the total time of determination can be reduced to equate with the "analyst" time.

EXPERIMENTAL

A range of materials, selected to cover the range of bulk production in the silica - alumina matrix, was analysed for alumina by both techniques. The coagulation technique was chosen for the removal of silica; 1-g samples were fused with 3 g of fusion mixture (potassium sodium carbonate) and 0.4 g of boric acid. The cooled melt was then dissolved in hydrochloric acid, evaporated for a few minutes and the silica coagulated with polyethylene oxide. The silica precipitate was then filtered, ignited, treated with hydrofluoric acid and the residue after ignition re-dissolved by fusion and added to the silica filtrate. The combined solutions were then made up to volume and an aliquot equivalent to 0.2 g withdrawn for the determination of alumina.

The aliquot was transferred to a separating funnel, further acidified and the iron and titanium removed by means of a cupferron - chloroform solvent extraction. After removing the excess of cupferron with chloroform washes, the solution was transferred to a conical flask for the determination of the alumina content.

Duplicate determinations were carried out, starting from separate fusions; two aliquots were taken from each solution and the iron and titanium removed. The first aliquot was transferred to a 500-ml conical flask and the alumina determined by using EDTA. In this method, the solution was neutralised to the change-point of bromophenol blue, excess of 0.05 M EDTA added and the solution buffered with ammonium acetate. The solution was then boiled for 10 minutes to ensure that the aluminium was completely complexed, cooled and the excess of EDTA back-titrated with standard zinc solution with dithizone as indicator. An almost equal volume of ethanol was added to ensure the solubility of the indicator.

The second aliquot was treated in a similar way, except that DCTA was used in place of EDTA. The reagent forms a complex with aluminium in the cold, so the solution was not boiled. As no reduction in volume due to boiling occurred, the aliquot was transferred to a 1-litre flask instead of the 500-ml flask used above and a roughly equal volume of ethanol added. This dissolved the traces of chloroform left behind from the cupferron separation and so avoided the risk that the dithizone indicator might be absorbed by the chloroform and thus cease to function.

One difficulty noted in the course of the experiments with DCTA was that when dithizone was added, the resulting green colour progressively disappeared and the solution turned orange - yellow. In this state, an end-point could not be distinguished. It was thought that this might be caused by the presence of traces of chloroform remaining from the solvent extraction, but experiments to simulate this condition showed that in synthetic solutions containing aluminium to which a few millilitres of chloroform had been added, no difficulty arose with the detection of end-points or with fading of the indicator. It was therefore concluded that this effect arose from traces of cupferron or its decomposition products left in the solution. Similar effects had been noticed with other indicators and had been thought to be from some form of oxidation of the indicator as the addition of hydroxylammonium chloride normally overcame the difficulty. In this connection, 10 ml of a 10 per cent. hydroxylammonium chloride solution proved to be completely effective in the determinations reported here. Subsequent work has, however, shown the desirability of increasing this addition to 20 ml, as on a few occasions the fading returned; no difficulty has been experienced when using the larger amount of hydroxylammonium chloride.

Both determinations were carried out and the results are shown in Table I. They show that the method appears to be sound for the determination of alumina in the range of silica - alumina materials.

TABLE I
DETERMINATIONS OF ALUMINA WITH EDTA AND DCTA AS COMPLEXING AGENTS
[BASED ON IGNITED (1000° C) SAMPLE]

Sample	Alumina content (Al_2O_3), per cent.			
	EDTA		DCTA	
	Results	Mean	Results	Mean
B.C.S. 314 Silica brick ..	0.91, 0.91	0.91	0.92, 0.92	0.92
C.A.S. 8 Feldspar ..	18.59, 18.67	18.63	18.63, 18.55	18.59
B.C.S. 269 Firebrick ..	34.10, 34.07	34.09	34.03, 34.06	34.05
B.C.S. 315 Firebrick ..	42.66, 42.64	42.65	42.61, 42.59	42.60
B.C.S. 309 Sillimanite ..	61.14, 61.14	61.14	61.13, 61.16	61.15
A.N. 29 Bauxite ..	88.48, 88.43	88.46	88.44, 88.34	88.39

The interference of calcium in the determination of alumina with EDTA is known to be overcome by the addition of sulphuric acid before the cupferron - chloroform extraction. (The interference appears to be eliminated by the presence of sulphate ion in the titration solution, but the use of sulphuric acid to replace a portion of the hydrochloric acid used to acidify the solution is a convenient way of achieving the required concentration.) When EDTA was replaced by DCTA, there was a possibility that this correction of the interference might no longer be valid. Synthetic solutions were used to demonstrate that calcium did not

interfere in the determination if sulphuric acid was used. Two solutions were used, one containing the equivalent of 50.05 per cent. of aluminium oxide alone and the other with 10 per cent. of calcium oxide. The results showed clearly that lime at the 10 per cent. level did not interfere in the determination of alumina in such materials as aluminosilicates, as 50.06 per cent. of aluminium oxide was found.

METHOD

DETERMINATION OF ALUMINA IN HIGH-SILICA, ALUMINOSILICATE AND ALUMINOUS MATERIALS

STOCK REAGENTS—

Reagents should be of analytical-reagent grade when available.

Acetic acid, glacial.

Ammonia solution, sp.gr. 0.88.

Bromophenol blue indicator.

Chloroform (B.P. grade).

Cupferron—If the reagent is coloured or gives a strongly coloured solution a new stock should be obtained. The reagent should be stored, together with a piece or pieces of ammonium carbonate to prevent decomposition, in a tightly stoppered bottle.

1,2-Diaminocyclohexanetetra-acetic acid (DCTA).

Dithizone.

Ethanol, 95 per cent. solution.

Hydrochloric acid, sp.gr. 1.18.

Hydroxylammonium chloride.

Naphthol green B, 0.1 per cent. aqueous solution.

Sodium hydroxide pellets.

Sulphuric acid, sp.gr. 1.84.

Zinc shot, 8 to 16 mesh.

PREPARED REAGENTS—

Ammonium acetate buffer—Add, with stirring, 120 ml of glacial acetic acid to 500 ml of water followed by 74 ml of ammonia solution (sp.gr. 0.88). Cool, dilute to 1 litre and mix.

Cupferron, 6 per cent. solution—Dissolve 1.5 g of cupferron in 25 ml of water and filter. This solution must be freshly prepared.

INDICATOR SOLUTIONS—

Bromophenol blue, 0.1 per cent. solution—Grind 0.1 g of bromophenol blue with 1.5 ml of sodium hydroxide solution (approximately 0.1 N) and then dilute to 100 ml with water and mix.

Dithizone, 0.025 per cent. solution—Dissolve 0.0125 g of dithizone in 50 ml of 95 per cent. ethanol. This solution will keep for about 1 week.

STANDARD SOLUTIONS—

1,2-Diaminocyclohexanetetra-acetic acid (DCTA), approximately 0.05 M—Dissolve 18.2175 g of DCTA in 500 ml of water by the progressive addition of the minimum amount of sodium hydroxide. Dilute to 1 litre in a calibrated flask and mix. Store in a polythene bottle. Standardise against the standard zinc solution.

Zinc solution, 0.05 M—Wash the metal first in hydrochloric acid (1 + 9) to remove any oxide film on the shot, then with water, alcohol and finally with ether. Dissolve 3.2685 g of the oxide-free metal in 10 ml of hydrochloric acid (sp.gr. 1.18) and about 50 ml of water; cover the beaker with a watch-glass and allow it to stand overnight on a steam-bath. Cool the solution and dilute it to 1 litre in a calibrated flask and mix.

1 ml of solution \equiv 2.55 mg of Al_2O_3 .

STANDARDISATION—

Transfer 50 ml of the 0.05 M DCTA solution to a 500-ml conical flask and add 5 to 6 drops of hydrochloric acid (sp.gr. 1.18). Add a few drops of a 0.1 per cent. bromophenol blue solution and add ammonium acetate buffer solution until the indicator turns blue. Then add 10 ml of buffer solution in excess.

Add a volume of ethanol equal to the total volume of the solution, followed by 1 to 2 ml of dithizone solution, and titrate with the standard zinc solution from blue to the first appearance of a permanent pink colour. Calculate the true concentration of the DCTA solution.

PROCEDURE—

The "stock" solution is that obtained after the removal of silica by the standard¹ or coagulation⁴ methods.

The standard method involves fusing 1 g of sample with 3 g of potassium sodium carbonate (for high-silica and aluminosilicates) or 1.5 g of potassium sodium carbonate and 0.2 g of boric acid (for aluminous materials), dissolving the melt in hydrochloric acid and dehydrating (adding sorbitol when boric acid is used) to precipitate the silica.

In the coagulation method a flux of 3 g of potassium sodium carbonate and 0.4 g of boric acid (high-silica and aluminosilicates) or 1.5 g of potassium sodium carbonate and 0.2 g of boric acid (aluminous materials) is used for a 1-g sample. The melt is dissolved in hydrochloric acid and evaporated until the silica gels or for 30 minutes, whichever is the quicker, and the silica precipitated with polyethylene oxide.

The silica is filtered off, ignited, weighed and treated with hydrofluoric and sulphuric acids. The residue is ignited, weighed, re-fused with potassium hydrogen sulphate and dissolved. The solution is added to the main filtrate from the silica to form the stock solution.

Separation of iron(III) oxide and titanium—For high-silica materials, transfer a 200-ml aliquot of the stock solution to a 500-ml separating funnel and add 40 ml of hydrochloric acid (sp.gr. 1.18). If the material is either known or suspected to contain a lime content equal to or more than the alumina content, add 30 ml of hydrochloric acid (sp.gr. 1.18) and 25 ml of diluted sulphuric acid (1 + 1) in place of the 40 ml of hydrochloric acid.

For aluminosilicates and aluminous materials, transfer a 100-ml aliquot of the stock solution to a 500-ml separating funnel and add 20 ml of hydrochloric acid (sp.gr. 1.18). If the material is suspected to contain more than about 5 per cent. of lime, add 10 ml of hydrochloric acid (sp.gr. 1.18) and 25 ml of diluted sulphuric acid (1 + 1) in place of the 20 ml of hydrochloric acid.

To the appropriate solution add 20 ml of chloroform and 10 ml of cupferron solution. Stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water.

Allow the layers to separate and withdraw the chloroform layer. Test that extraction is complete by checking that the addition of a few drops of cupferron solution to the aqueous solution does not produce a permanent coloured precipitate.

Add further 10-ml portions of chloroform and repeat the extraction until the chloroform layer is colourless. Discard the chloroform extracts.

DETERMINATION OF ALUMINA—

Run the aqueous solution from the cupferron - chloroform separation into a 1000-ml conical flask. Add a few drops of bromophenol blue indicator and add ammonia solution (sp.gr. 0.88) until just alkaline.

Just re-acidify quickly with hydrochloric acid (sp.gr. 1.18) and add 5 to 6 drops in excess.

Add sufficient standard DCTA solution to provide an excess of a few millilitres over the expected amount. Then add ammonium acetate buffer solution until the indicator turns blue, and add 10 ml in excess.

Add an equal volume of ethanol, 20 ml of hydroxylammonium chloride solution (10 per cent.) and 1 to 2 ml of dithizone indicator, and titrate with standard zinc solution from green to the first appearance of a permanent pink colour. (The end-point is often improved by the addition of a few drops of naphthol green solution to eliminate any pink colour that may be formed in the solution on the addition of the indicator.)

Calculation—If the DCTA solution is not exactly 0.05 M, calculate the equivalent volume of 0.05 M DCTA.

If V ml is the volume of DCTA and v ml is the volume of standard zinc solution used in the back-titration, then

Al_2O_3 , per cent. = 1.275 ($V-v$) for a 100-ml aliquot
and Al_2O_3 , per cent. = 0.6375 ($V-v$) for a 200-ml aliquot.

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oxidation of the solution with nitric acid (sp.gr. 1.42) and evaporation to fumes of sulphuric acid; this modification was subsequently applied to all samples.

Some of the samples containing yttrium in excess of 1 per cent. were also analysed by a gravimetric method involving a double precipitation of yttrium hydroxide, followed by precipitation of yttrium fluoride, conversion of the fluoride into soluble perchlorate, a further precipitation of yttrium hydroxide and final determination of the yttrium as oxide (Y_2O_3) (unpublished work by this Department).

Results of these tests are given in Table I.

CONCLUSIONS

Tests have shown that a method based on spectrophotometric measurement of the blue-coloured complex formed by the reaction of yttrium ions with arsenazo III in a solution at pH 2.5 can be applied to the determination of 50 p.p.m. to about 4 per cent. of yttrium in chromium. Yttrium must first be separated from chromium(VI), and this is achieved by the precipitation of yttrium hydroxide from an ammoniacal chloride solution by using aluminium hydroxide as a "collector."

Interference from the added aluminium, which also reacts with arsenazo III, can be prevented by forming a stable, colourless aluminium - sulphosalicylic acid complex before developing the yttrium - arsenazo III complex.

Iron(III) interferes but, based on a 0.2-g sample, up to 1 per cent. of iron can be tolerated, provided it is reduced to iron(II) with ascorbic acid before the final colour is developed. Titanium, zirconium and hafnium form coloured complexes with arsenazo III and also suppress development of the yttrium - arsenazo III complex, but a preliminary separation of these metals based on precipitation with phenylarsonic acid enables the proposed method to be applied to the determination of yttrium in chromium-base alloys containing up to 5 per cent. of titanium, zirconium or hafnium (based on a 0.2-g sample). Niobium and tantalum are precipitated with yttrium in the ammoniacal chloride solution, but on digestion of the mixed hydroxides with hot dilute nitric acid, niobium and tantalum are separated as insoluble earth acids and can be removed effectively by filtration.

Based on a 0.2-g sample, the presence of 5 per cent. of manganese, molybdenum, nickel, silver or tungsten, 1 per cent. of copper, 0.5 per cent. of cadmium, lead or zinc, 500 p.p.m. of iron, 250 p.p.m. of hafnium, tin, titanium or vanadium, or 50 p.p.m. of zirconium in the final solution has no significant effect on the absorbance.

Tartrate, citrate, oxalate, fluoride and EDTA inhibit formation of the yttrium - arsenazo III complex.

The pH value and concentration of the reagents must be carefully controlled because variations of either affect the absorbance. The recovery of yttrium obtained by the hydroxide precipitation is about 97 per cent. and, to obtain optimum precision, it is recommended that the final absorbance of the sample solution should be related to the absorbance obtained on standard solutions of yttrium that have been simultaneously examined by the entire procedure.

By using the proposed method a batch of about six samples can be completed in a normal working day.

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Electronic Modulation of Electrodeless Discharge Tubes for Use in Atomic Spectroscopy

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A system for effecting modulation of the light output from microwave-excited discharge tubes by purely electronic means is described. The system is thought to have some advantages over the use of a mechanical chopper, and can be applied to instruments into which a chopper cannot be fitted.

MUCH of the work reported on the technique of atomic fluorescence has been carried out by using low temperature, low spectral background flames such as air - hydrogen or air - propane, which allow the use of a simple method such as that with unmodulated light sources and d.c. amplification.^{1 to 7} Unfortunately, such flames have too low an energy content for use when the element under investigation is contained in a large amount of matrix, and the use of the higher temperature air - acetylene or nitrous oxide - acetylene flame becomes mandatory if adequate volatilisation of the matrix and atomisation of the sought element is to be obtained. These flames have the disadvantage that they give considerable emission themselves in the ultraviolet and visible parts of the spectrum, and this background reduces the signal-to-noise ratio considerably in the fluorescence technique. The same problem is, of course, encountered in atomic-absorption spectroscopy, and has been solved by the use of modulated light sources and a.c. amplifiers. In this instance, the fluctuations in the flame background become much less important and cease to be the limiting factor in determining the sensitivity that can be attained; this now depends on other factors such as the monochromator aperture, the noise levels of the detector and measuring circuitry.

In atomic-absorption work, the most commonly used source is the hollow-cathode lamp, but for fluorescence work, in which the sensitivity obtainable is directly proportional to the incident light intensity, the use of the intense microwave-excited electrodeless discharge tube has much to recommend it. These tubes have been used with mechanical choppers to effect modulation, but this method has certain disadvantages; it has been found necessary in our laboratory to move the source away from the flame so as to be able to fit the chopper between the two, which reduces the light intensity reaching the flame according to the inverse square law. In addition, operation of the chopper close to the flame can lead to atmospheric turbulence and flame instability, and there is often difficulty in designing a mechanical system to operate consistently under the adverse conditions of high temperature and humidity found in the flame compartment. These difficulties will depend on the type of instrument used, but with most commercially available atomic-absorption spectrophotometers the use of mechanical choppers is avoided and electronic modulation of the light source used. This can introduce a further difficulty if a modified atomic-absorption spectrophotometer of this latter type is to be used for atomic-fluorescence work, as it is often difficult to synchronise the phase-sensitive detectors used with a mechanical chopper.

In view of the above difficulties, it was decided to investigate the possibility of modulating microwave discharge tubes electronically, and to assess their use for atomic spectroscopy when thus modulated.

EXPERIMENTAL

APPARATUS—

A Southern Analytical A3000 atomic-absorption spectrophotometer, modified for fluorescence, was used. The modification enabled the instrument to accept modulated light signals as in the normal absorption mode, but removed the logarithmic converter from the measurement system. Results were thus free from the effect of continuous light emission from the flame, and were presented linearly proportional to light intensity.

The primary microwave generator was a Microtron 200 instrument, used with a smoothing unit and a reflected power meter, all of which were obtained from Electro-Medical Supplies Ltd. The modulation unit available from this source was not suitable for our purpose, as it was not compatible with the A3000 phase-sensitive detector, and the generator was therefore modified.

The modulation signal was generated by a free-running symmetrical multi-vibrator, which operated at a frequency that could be varied between about 180 and 330 Hz. This was transformer-coupled into the anode circuit of the magnetron, with an eleven-position switch providing variable attenuation of the multi-vibrator output into the transformer primary coil, so that the depth of modulation of the magnetron anode current could be altered between 25 and 75 per cent. The operating frequencies used in this work are too low to permit 100 per cent. modulation of a microwave discharge tube, but were chosen to be compatible with the A3000 amplifiers.

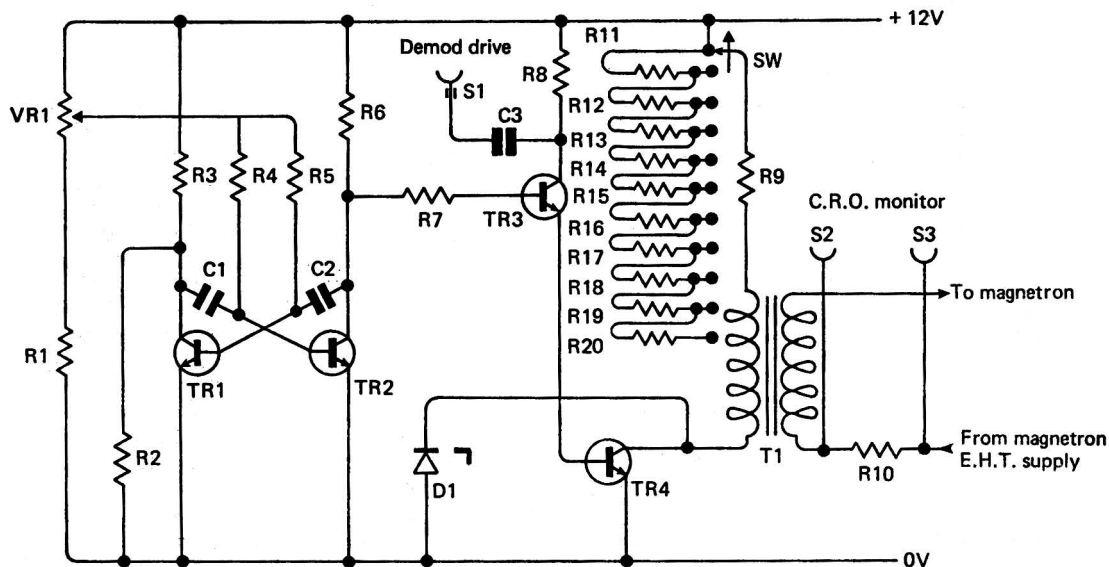


Fig. 1. Experimental modulator unit (for list of components, see Appendix, p. 566)

The experimental circuit is shown in Fig. 1. The actual depth of modulation of the magnetron anode current is shown below, but the modulation achieved on the light output of the microwave tubes varied with tube type and operating characteristics as described later.

Switch position	1	2	3	4	5	6	7 to 11
Percentage modulation	25	30	40	50	60	70	75

CAVITY—

Two cavities were used, the 214L and the 210L, both being obtained from Electro-Medical Supplies Ltd. The 214L cavity was found to be unsatisfactory as there was considerable electronic interference with the A3000 amplifiers, probably because of pick-up of stray microwave radiation. In addition, tuning of the 214L cavity was critical, and its shape is such that large amounts of the incident light were reflected into the monochromator unless an intricate system of baffles was used.

The 210L cavity was modified by enlarging the viewing aperture to a depth of 1 inch and a width of $\frac{5}{8}$ inch and fitting a cooling air inlet to the base; a copper-tube cooling ring was also fitted around the co-axial gap adjuster, so that tubes could be cooled either from the top or bottom when in operation. No electrical interference was encountered with this cavity, provided that the tube did not extend outside the cavity, and reflection of the incident light into the monochromator was negligible.

The cavity was mounted on the optical shelf of the A3000, with its vertical axis 42 mm from the centre of the flame. Tubes were mounted in the cavity by fitting a rubber grommet

over the tube so that the grommet rested on the upper rim of the co-axial gap adjuster. A front-aluminised mirror was placed in the burner position to reflect the light from the tubes into the monochromator entrance slit, so that direct measurement of intensity and stability could be made.

PREPARATION OF TUBES—

The method used for the preparation of tubes for use in the 210L cavity broadly follows that already described for preparing tubes for use in the 214L cavity^{4,5,6,7}; the main difference is that the optimum argon pressure for the larger cavity is about 3 torr, as opposed to 1 torr used in the earlier work. Iodine was not heated at the de-gassing stage of the preparation but merely pumped at about 0.1 torr for 2 minutes to remove any surface-moisture film; the iodine-to-metal ratio was not found to be critical for most of the tubes used in this work, except for tin and lead. For these two elements, the ratio for tin to iodine must lie between 1:2 and 1:4 and that for lead to iodine between 1:1 and 1:2 if satisfactory discharges are to be obtained.

POSITIONING OF TUBES—

It was found necessary to differentiate between tubes containing volatile elements or compounds and the tubes with less volatile contents when considering how to position them in the cavity. "Volatile" in this context is taken to mean exerting a vapour pressure of more than about 1 torr at 300°C, and "involatile" as exerting a lower vapour pressure. Volatile elements were antimony, arsenic, tin, iodine and mercury; involatile elements were cadmium, zinc, selenium, tellurium, cobalt and lead. The main difference lies in the way in which the tube is maintained at operating temperature in the cavity; for volatile materials, the filling material was first sublimed by external heating so that it collected at the bottom of the tube proper. It was then positioned in the cavity so that the bottom of the viewing aperture came about half-way up the tube. The bottom part of the tube thus extended well into the internal cylinder within the cavity, and the tube ran relatively cool with the filling material remaining at the bottom. Cooling air was directed up the centre of the cavity, and thus flowed around the entire body of the tube; the degree of cooling required depended on the volatility, with iodine tubes needing by far the most. It was sometimes found that "volatile" tubes were much easier to initiate without modulation, the modulation being switched on when the tube had attained operating temperature.

For tubes with involatile filling materials the optimum mounting position was with the bottom of the tube only 2 mm below the lower edge of the viewing aperture, *i.e.*, extending into the internal cylinder by only this amount. These tubes were again heated prior to use, but in this instance to drive the filling material to the top of the tube by sublimation. It should remain there during operation, and this is ensured provided the bottom of the tube is not allowed to enter too far into the internal cylinder.

If "involatile" tubes were operated with the wrong conditions for this type, only an argon discharge was obtained and the depth of modulation decreased rapidly. For substances of moderate volatility, such as selenium or tellurium, the "involatile" conditions were used and cooling applied to the top of the tube via the ring of copper tubing fitted there.

The operating conditions used for the tubes investigated are shown in Table I.

TABLE I
OPERATING CONDITIONS

Element	Wave-length, nm	Optimum power, W	Reflected power, W	Switch position	Modulation of resonance line, %	Cooling
Cadmium ..	228.8	50	23	8 to 11	41	None
Zinc ..	213.9	55	25	8 to 11	55	None
Selenium ..	196.1	25	6	8	72	Top
Tellurium ..	214.3	25	5.5	6	75	Top
Cobalt ..	240.7	55	4	6	58	None
Lead ..	283.3	50	22	7 to 9	67	None
Antimony ..	231.1	30	6	7	83	Very slight bottom
Arsenic ..	193.7	30	11	7	85	Very slight bottom
Tin ..	286.3	35	6	5	73	Moderate bottom (critical)
Mercury ..	253.7	30	8	7	70	Moderate bottom

MEASUREMENT OF DEGREE OF MODULATION—

The depth of modulation of the light output from a tube was found not to be proportional to the depth of modulation of the microwave envelope, and it was decided to measure the true modulation achieved. This was accomplished by applying both the output of the modulator oscillator and the output of the photomultiplier to the two input channels of a double-beam oscilloscope. In this way the relative modulation depths could be measured, and it could be seen at a glance if any phase shift had occurred. If this had taken place, the response from the photomultiplier would not have been synchronised with the phase-sensitive detector, and the sensitivity would have been seriously impaired.

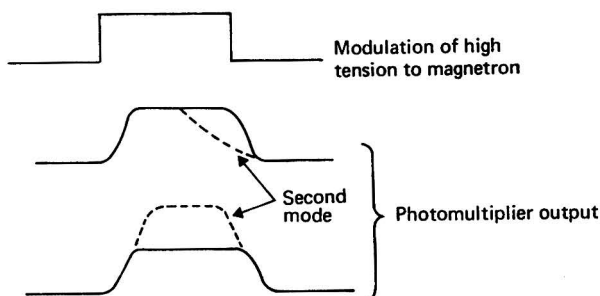


Fig. 2. Two-mode wave form

At no time was any phase shift noted, but the onset of instability with volatile substances, particularly iodine, showed as a cyclic variation in the depth of modulation (Fig. 2). This effect was also noted with arsenic, mercury, antimony and tin tubes when they were run at high temperatures, but these elements could be maintained in a stable condition by suitable choice of operating power and cooling. It was not found possible to run an iodine tube both modulated and stable, although such tubes were stable when unmodulated. This possibly results in part from the instability of magnetron tubes at the low powers needed for iodine tubes, and partly from inability of the output to follow the modulation at the higher pressures that build up in these tubes. Increasing the power applied to an iodine tube led to a decrease in the depth of modulation; at 30 W there was no modulation, and at 35 W the intensity decreased. As the power was further increased, the intensity decreased still further. This effect is also thought to be caused by pressure build-up in the tube. An experimental tube containing only a trace of iodine and 3 mm of argon did not exhibit this effect; unfortunately, it is not practicable to use tubes of this type for normal work as the intensity of the output is about thirty times lower than that for normal tubes.

CONCLUSIONS

It is possible to operate microwave-excited discharge tubes in the modulated mode in a manner similar to hollow-cathode lamps, but the conditions for successful results are much more stringent and close attention must be paid to operating conditions. More than thirty tubes were studied in this work, and with the exception of the iodine tubes all could be successfully modulated; most of them exhibited similar characteristics when modulated, and it seems likely that these characteristics are general for tubes of a similar type to ours when used in similar equipment.

The three-quarter-wave 210L cavity was found to be the most suitable for modulated operation; optimum gas pressure was about 3 mm, tubes at 1 mm pressure tending to be extinguished when modulated, and tubes at 6 mm showing slightly decreased intensity.

The efficiency of operation is critically dependent on the vertical positioning of the tube in the cavity, the operating power, the depth of modulation of the microwave power and the degree and type of cooling applied to the tube. The stability of most tubes was similar, whether operated while modulated or unmodulated, with a slight improvement in stability for volatile elements when unmodulated. The output intensity was found to be more sensitive to variations in power, positioning and cooling when modulated than when unmodulated.

The behaviour of the tubes was not affected by variations in the frequency of modulation over the range 180 to 330 Hz; all measurements made in this work were at 180 Hz. Their behaviour is, however, affected by the amount of metal in the tube, and larger amounts make successful modulation more difficult to achieve.

The authors thank the Directors of Southern Analytical Limited for permission to publish this work, and Mr. J. G. Barrell who designed and built the experimental electronic equipment.

Appendix

LIST OF COMPONENTS

R ₁	= 1.5-k Ω resistor
R ₂ , R ₇	= 1.8-k Ω resistors
R ₃ , R ₆	= 2.7-k Ω resistors
R ₄ , R ₅	= 100-k Ω resistors
R ₈	= 220- Ω resistor
R ₉	= 12- Ω resistor
R ₁₀	= 10- Ω resistor
R ₁₁ , R ₁₂	= 1- Ω resistors
R ₁₃	= 2.2- Ω resistor
R ₁₄	= 6- Ω resistor
R ₁₅	= 13.5- Ω resistor
R ₁₆	= 24- Ω resistor
R ₁₇	= 30- Ω resistor
R ₁₈	= 60- Ω resistor
R ₁₉	= 75- Ω resistor
R ₂₀	= 135- Ω resistor
VR ₁	= 500- Ω variable resistor
C ₁ , C ₂	= 40-nF capacitors
C ₃	= 100-nF capacitor
TR ₁ , TR ₂ , TR ₃	= BC108 transistors
TR ₄	= BFY50 transistor
D ₁	= BZX61-C75 diode
T ₁	= Transformer (1:3)
S ₁	= Screened socket
S ₂ , S ₃	= Sockets
SW	= Eleven-position switch

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The Interference of Cobalt, Nickel and Copper in the Determination of Iron by Atomic-absorption Spectrophotometry in an Air-Acetylene Flame

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An investigation of interferences in the determination of iron by atomic-absorption spectrophotometry in an air-acetylene flame is reported. It has been found that three elements, cobalt, nickel and copper, exhibit serious depressive effects, the magnitude of which is strongly dependent on the flame conditions, with respect to both fuel-to-air ratio and the height of the optical path above the burner, and is also dependent on the anion present in the sample solution. The optimisation of the flame for both pure iron solutions and those containing the interfering elements, and means of suppressing these interferences, are discussed. The use of 8-hydroxyquinoline at a concentration equal to or greater than the total concentration of cobalt, nickel and copper is recommended as an effective releasing agent.

NUMEROUS papers have described the determination of iron by atomic-absorption spectrophotometry in a wide variety of materials and these have been collated by several authors.^{1,2,3} In low temperature flames some interference effects have been reported, but silica is the only recorded interference when an air-acetylene flame is used,² despite several fairly detailed investigations.^{4,5} This has led to the conclusion drawn, for example, by Slavin,² that "iron determinations (by atomic-absorption spectroscopy) are almost free from any interference when a stoichiometric air-acetylene flame is used," which is in marked contrast to the determination of elements such as magnesium and calcium. In these latter cases, interference effects are marked, and have in general been explained by the formation of oxide molecules or compounds which exhibit degrees of dissociation different from those of the original oxide species.^{6,7,8,9}

In this laboratory, we have recently been investigating the interference effects observed in the atomic-absorption determination of a number of transition elements (Rowston, W. B., unpublished results).^{10,11} Despite earlier contentions, many interference effects have been recorded and are almost as prevalent under certain operating conditions as those found for calcium and magnesium. For example, under the optimum flame conditions for the analytical determination of iron and in a sulphate or nitrate medium, cobalt, nickel and copper have shown significant interference effects and these are described in this paper. Possible ways of suppressing these interferences are also discussed.

Other elements exhibit smaller interference effects under the same conditions and these effects may be enhanced under other non-ideal analytical conditions. An intensive study of these phenomena in a variety of flames and conditions is in progress and will be reported in a subsequent paper.

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EXPERIMENTAL

During the course of this work three different commercially available instruments were used without modification, and the sources were the normal hollow-cathode lamps supplied with each instrument. The optimum working conditions, *i.e.*, those giving maximum absorption for a pure iron solution, are given in Table I for all three instruments. Working conditions were varied from time to time as described in the text.

TABLE I
OPTIMUM WORKING CONDITIONS FOR THE ATOMIC-ABSORPTION DETERMINATION OF IRON

	Unicam SP90	Perkin-Elmer 303	Perkin-Elmer 290
Wavelength, nm	248.3	248.3	248.3
Lamp current, mA	20	30	10
Slit width setting	0.1 mm	0.2 mm	0.2 mm
Height of optical path above burner, mm	10	10	8 to 10
Acetylene flow-rate, l minute ⁻¹	1.38*	9.0*	3.45†
Air flow-rate, l minute ⁻¹	5*	9.0*	9.9†
Burner path length, mm	100	100	50

* Instrument flow-meter readings at recommended gas-feed pressures.

† Rates corrected to atmospheric pressure. Equivalent to flow-meter readings of 13.85 for acetylene and 14.00 for air, at gas-feed pressures of 8 p.s.i.g. of acetylene and 35 p.s.i.g. of air.

Emission spectra of iron(II) oxide were measured with the Perkin-Elmer 290, fitted with the flame-emission accessory.

All solutions were prepared from the purest readily available chemicals, and checks were made to ensure that impurities of iron in any reagent did not contribute to the absorption reading. Considerable care was taken to avoid introducing into the solution any anions other than the one of interest, as it was felt that considerable uncertainty might result if, say, a metal chloride solution was used to study the effect of other anions. For example, when the effect of an interference was being investigated in a sulphate medium, all the metal salts were taken as sulphates and sufficient dilute sulphuric acid was added to ensure dissolution. At the concentrations used, and in the absence of any other metal ions, similar absorbances were obtained from solutions of iron(III) in hydrochloric, sulphuric and nitric acids. Differences were observed immediately particular metal ions were added to these solutions, and these are described in the text.

The output meter of the Unicam SP90 is calibrated in absorbance units and the Perkin-Elmer 303 and 290 in percentage absorption. Readings are reported in the units in which they were measured with a particular instrument. This may at first sight appear to be confusing, but within each set of results the values are relative and related to the "absorbance" of a pure iron solution measured under optimum conditions. The units are therefore of no consequence. The results were found to be readily reproducible on any of the instruments.

RESULTS AND DISCUSSION

OPTIMUM FLAME CONDITIONS—

When a pure iron solution was sprayed into an air - acetylene flame it was found that maximum absorption occurred when the light path was 8 to 10 mm above the top of the burner with the flame burning under slightly fuel-lean conditions. These observations are in agreement with the conditions recommended by other workers for analysis,^{12,13} but require further elucidation. The absorption signal is strongly dependent on burner height as can be seen from curve A in Fig. 3, and care must be taken to obtain a reproducible and permanent position of the burner with respect to the light beam.

The effect of varying the fuel-to-air ratio was found to be different in sulphate (or nitrate) compared with chloride medium, as shown by curves A and B of Fig. 1. An estimate, based on calculation, of the position of stoichiometric composition is also shown for reference purposes. The calculation supported visual conclusions of stoichiometry based on the appearance of incandescent carbon particles, which occurs at acetylene flow-rates of 4.20 l minute⁻¹ and above. Starting with a very lean flame, the absorbance increases gradually with increase in acetylene flow-rate. This could be explained by the enhanced dissociation of iron(II) oxide, which is to be expected as the effective concentration of oxygen decreases

with increase in acetylene flow-rate. Confirmation of this hypothesis was obtained by observation of the iron(II) oxide band emission at 574 nm,¹⁴ which was found to decrease linearly with increase in acetylene flow-rate over the entire range shown in Fig. 1. However, the iron-atom absorption does not entirely correspond to the gradual loss of iron(II) oxide emission, as it reaches a maximum at 3.45 l minute⁻¹ and then falls off rapidly in a sulphate or nitrate medium, becoming almost zero in a very fuel-rich flame. In contrast, in a chloride medium, the absorption signal is maintained up to a fairly rich flame mixture after which a gradual fall off occurs due, presumably, to the decrease in flame temperature and dilution of the flame gases with the excess of acetylene under these conditions. The sharp fall in iron absorption in sulphate or nitrate medium indicates depopulation of ground-state atoms, presumably either by the formation of a compound less easily dissociated than iron(II) oxide, or by abnormal excitation to higher energy levels.

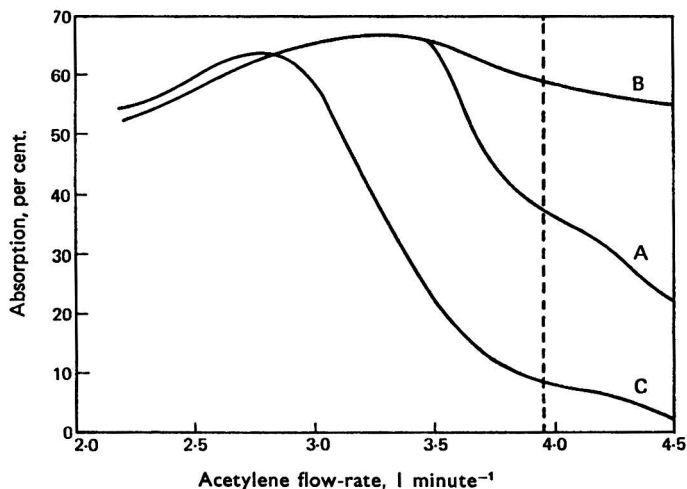


Fig. 1. Variation of the atomic-absorption signal of 25 p.p.m. of iron(III) with rate of acetylene flow. Air flow 9.9 l minute⁻¹, optical path centred at 9 mm above the top of the burner. Rates of both gases corrected to atmospheric pressure. Curve A, in the presence of 10⁻³ M hydrochloric acid; curve B, 10⁻³ M sulphuric acid; curve C, containing 200 p.p.m. of cobalt in 10⁻³ M sulphuric acid. Approximate position of stoichiometric fuel-to-air ratio indicated by dotted line. Instrument PE290

The careful optimisation of flame conditions is thus more important in a sulphate or nitrate medium than in chloride, but in general a slightly fuel-lean flame gives maximum sensitivity in all three cases.

INTERFERENCE OF COBALT, NICKEL AND COPPER—

Under the optimum conditions described above, a wide range of anions, cations and complexing agents was investigated as possible interferences in the atomic-absorption determination of iron.¹⁰ Experiments were conducted at two concentrations of iron (10 and 20 p.p.m.) and at at least two concentrations of each added ion. Apart from cobalt, nickel and copper no significant depressive effects were observed at ionic concentrations as high as 5000 p.p.m. In particular, other cations such as chromium(III), manganese(II), zinc, magnesium and aluminium showed little interference under the above conditions. Mineral acids such as hydrochloric, sulphuric, nitric, perchloric and phosphoric acids also showed only small interferences at concentrations up to 5 per cent. The effect of organic solvents was investigated and the results were in substantial agreement with those reported by Atsuya¹⁵ and are, therefore, not discussed further.

Under the optimum analytical conditions it appeared that cobalt, nickel and copper were the most significant interferences and their effects were subjected to more detailed study. The effects of all three elements are remarkably similar, and the variation of absorption with variation in concentration of interfering element is illustrated for nickel in Fig. 2. Cobalt and copper are similar in effect to nickel but show slight variations in the magnitude of the depression. A strong dependence on the nature of the acid or anion present is observed, as in hydrochloric acid a much smaller depressive effect occurs compared with sulphuric and nitric acids, in which all three elements have a strong depressive effect that reaches a maximum at about 100 p.p.m. of cobalt, nickel or copper. This behaviour has been observed on previous occasions and the interference of aluminium on the determination of magnesium has been shown¹ to exhibit a similar dependence on the anion present in solution.

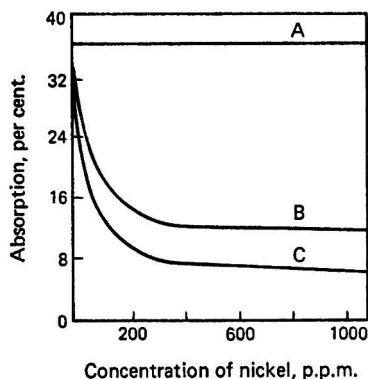


Fig. 2. Interference of nickel on the atomic-absorption signal of 10 p.p.m. of iron(III). Conditions as described in Table I (PE303). Curve A, hydrochloric acid medium; curve B, sulphuric acid medium; curve C, nitric acid medium

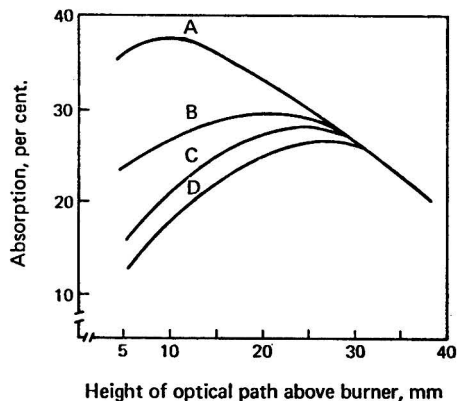


Fig. 3. Effect of the height of the optical path above the top of the burner on the interference of nickel in 0.01 M sulphuric acid medium on the atomic-absorption signal of 10 p.p.m. of iron(III). Concentration of nickel: curve A, 0 p.p.m.; curve B, 50 p.p.m.; curve C, 100 p.p.m.; curve D, 1000 p.p.m. Other experimental conditions as in Table I (PE303).

The interference effects disappear at higher parts of the flame (Fig. 3). Curve A shows the marked dependence of the iron signal on the part of the flame under examination and the decrease in signal at higher parts of the flame corresponds to an increase in emission from iron(II) oxide. Addition of various amounts of nickel in a sulphuric acid medium shows strong interference at 10 mm consistent with Fig. 2, but at higher positions in the flame the interference disappears and all the curves become more or less identical with curve A at a flame height of 30 mm above the burner. Copper and cobalt showed similar behaviour, except that the exact height above the burner at which the interference disappeared varied slightly. This phenomenon could only be observed with the Perkin-Elmer 303, as neither of the other instruments permitted the use of the higher optical paths.

When the effect of flame composition was investigated in the presence of cobalt, nickel and copper, curve C in Fig. 1 was obtained. Under the optimum analytical conditions of $3.45 \text{ l minute}^{-1}$, strong depression of the signal is indicated and this is found at all acetylene flow-rates greater than 3 l minute^{-1} . However, in an extremely fuel-lean flame, the depression is removed and a slight enhancement of about 4 per cent. is observed. It has been suggested¹² that the interference caused by nickel may be overcome by the use of a strongly fuel-lean air-acetylene flame, but this may not be acceptable in view of the enhancement noted here, which was perfectly reproducible, and could not be ascribed to impurities in the reagents.

While a detailed explanation of these interferences will be left to a subsequent paper in which more evidence will be presented, it appears that cobalt, nickel and copper must enter into some kind of chemical or physical reaction with iron either during the decomposition

and dissociation of the dehydrated metal salts or "clots," or with the metallic vapour after it is formed. The flame profile patterns of the interferences, for example with respect to flame height, suggest that the latter is unlikely. In addition, the disappearance of the interferences in an extremely fuel-lean flame suggests that the mechanism of these interferences may be different from the oxide or mixed oxide formation proposed in order to explain some other cationic interference phenomena.^{6,7,8,9,16,17}

SUPPRESSION OF INTERFERENCES—

The use of an extremely fuel-lean flame could not be considered as an entirely satisfactory method of removing the interference of cobalt, nickel and copper when high precision is required, because of the enhancement noted above. The addition of cobalt, nickel or copper to the iron standards would be satisfactory for a fuel-lean flame (acetylene flow-rate < 2.8 l minute⁻¹, see Fig. 1) but much less satisfactory for the optimum flame conditions outlined earlier, when a considerable loss in sensitivity would result (Figs. 2 and 3). A higher position in the flame could be used, but besides a loss in sensitivity this would suffer from the additional disadvantage that small variations in the height above the burner would either introduce errors in the determination or necessitate more frequent calibration of the instrument.

The simplest means of overcoming the interference effects would be to prepare all solutions in a hydrochloric acid medium, but even this introduces a slight depression of the signal, which increases with increase in the concentration of interfering ion in the solution. The presence of chloride ions obviously offers an alternative mechanism for the production of iron atoms, which may be similar to that proposed for magnesium,⁶ and the small residual depression is presumably caused by the fact that the chloro complexes of iron are weak.¹⁸ The effect of the addition of chloride (as sodium chloride) on the interference of 200 p.p.m. of cobalt on 10 p.p.m. of iron in sulphuric acid medium was investigated and it was found that the signal was not completely restored to that obtained in the absence of cobalt even in the presence of 2 M chloride ions.

TABLE II
EFFECT OF VARIOUS RELEASING AGENTS ON THE INTERFERENCE OF NICKEL ON
THE ATOMIC-ABSORPTION SIGNAL OF 25 P.P.M. OF IRON (SP90)

Releasing agent	Absorbance		
	Without nickel or releasing agent	In the presence of 1200 p.p.m. of nickel	In the presence of 1200 p.p.m. of nickel and the releasing agent
Calcium, 4.2×10^{-2} M	0.142	0.064	0.144
Strontium, 3.5×10^{-2} M	0.142	0.064	0.144
Barium, 3.8×10^{-2} M	0.142	0.064	0.143
8-Hydroxyquinoline, 1.03×10^{-2} M	0.149	0.064	0.149

Chloride being inadequate, other releasing agents were sought and the use of 8-hydroxyquinoline, strontium, calcium or barium was found to be suitable. Some typical results for nickel are shown in Table II and similar results have been obtained for cobalt and copper. However, subsequent investigations¹⁹ have shown that the effects of elements such as calcium are strongly dependent on flame conditions and on the relative concentration of interfering and releasing agents, and their use is not recommended. By far the most convenient releasing agent we have encountered is 8-hydroxyquinoline and solutions containing 5 per cent. of 8-hydroxyquinoline were found to overcome the interference from up to 1000 p.p.m. of cobalt, nickel or copper.

The releasing action of 8-hydroxyquinoline was subjected to more detailed investigation and it was found that the concentration required to remove the interference effect was directly proportional to the concentration of cobalt, nickel or copper present in the solution. This effect resembles that described by Wallace²⁰ for the releasing action of 8-hydroxyquinoline on the interference of aluminium in the determination of magnesium in an air-propane flame. However, when the concentration of complexing agent was varied a different pattern was observed. At low concentrations, 8-hydroxyquinoline has no releasing effect on the interference and the absorbance only begins to increase at an 8-hydroxyquinoline concentration equal to one sixth of the concentration of cobalt present in the solution (Fig. 4). At

twice this concentration the interference is more or less removed, but the original absorbance, measured in the absence of cobalt and 8-hydroxyquinoline is attained only at about a 1:1 ratio of cobalt to 8-hydroxyquinoline. In Fig. 4, two "end-points" (A and B) can be discerned and variation in the concentration of cobalt or nickel present always gave similar "end-points" at ratios of cobalt to 8-hydroxyquinoline of 6:1 and 3:1, respectively. The direct proportionality is illustrated in Fig. 5, in which the concentrations of 8-hydroxyquinoline required to reach the points A and B are plotted against the cobalt concentration. Varying the concentration of iron had little or no effect on the position of A and B but merely moved the curve in Fig. 4 up or down the absorbance axis.

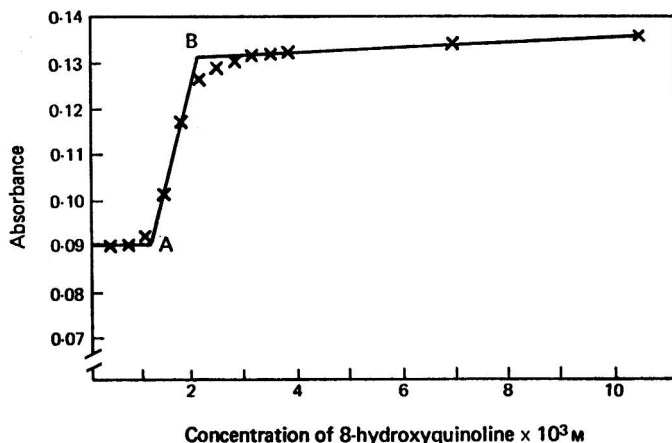


Fig. 4. Effect of the concentration of 8-hydroxyquinoline on the interference of 400 p.p.m. (6.79×10^{-3} M) of cobalt on the atomic absorption of 25 p.p.m. of iron. Note two "end-points" A and B. Instrument SP90

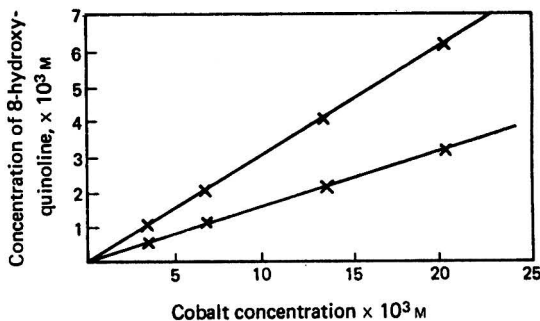


Fig. 5. Dependence of the concentration of 8-hydroxyquinoline required to reach the points A and B on Fig. 4, on the concentration of cobalt present (SP90)

Although the use of either a fuel-lean air - acetylene flame or the addition of, for example, calcium, will remove the interference of cobalt, nickel and copper in the atomic-absorption determination of iron in a sulphate or nitrate medium, the addition of 8-hydroxyquinoline is recommended. The concentration of 8-hydroxyquinoline should be equal to or greater than the total concentration of cobalt, nickel and copper present in the solution.

We thank the Chemistry Departments of the Stow College of Engineering and the Paisley College of Technology for permission and facilities for the use of their atomic-absorption spectrophotometers, and one of us (D.R.B.) gratefully acknowledges the support of a Colombo Plan Scholarship together with the grant of study leave from the Nepal Geological Survey. The purchase of our own atomic-absorption spectrophotometer was made possible by the award of an S.R.C. research grant, which is also gratefully acknowledged.

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Evaluation and Correction of Interference between Aluminium, Silicon and Iron in Atomic-absorption Spectrophotometry

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Inter-element interference in the determination of aluminium, silicon and iron in pyrophosphate solutions has been investigated. The maximum concentrations were 100 p.p.m. of aluminium, 117 p.p.m. of silicon and 50 p.p.m. of iron; the tetrasodium pyrophosphate was 7.5×10^{-3} M. In the determination of aluminium, silicate depressed the absorption, while iron did not interfere. Both aluminium and iron enhanced the absorption in the determination of silicon, and in the determination of iron, both aluminium and silicon depressed the absorption. Absorbance data, representing analytical results on some 215 solutions, were fitted to equations containing so-called interference coefficients. With this approach, corrections for inter-element interference are easily made.

As part of a study of the interaction between kaolin and tetrasodium pyrophosphate solutions, it became necessary to analyse a large number of filtrates for the elements aluminium, silicon and iron. The anticipated maximum concentrations of each element were 100 p.p.m. of aluminium, 117 p.p.m. of silicon (*i.e.*, 250 p.p.m. of silica) and 50 p.p.m. of iron. Tetrasodium pyrophosphate concentrations were about 7.5×10^{-3} M and the solutions (pH range mainly from 6 to 8) contained additional sodium and mere traces of other elements.

Atomic absorption was chosen as the analytical tool because of its facility for rapid throughput and because only relatively small volumes of solution were available. The literature^{1 to 7} provides little detail on the actual magnitudes of such inter-element interferences as may occur in analysing the above solutions. Perhaps the most detailed study is that by Price and Roos¹ who, by using separate additions, showed that silicon absorbance was enhanced by iron and by aluminium and depressed by phosphate. Interference by silicate in the determination of iron has been reported.⁶

A detailed study of the inter-element interference has been made by analysing about 200 solutions (7.5×10^{-3} M in tetrasodium pyrophosphate) containing known amounts of aluminium (0 to 100 p.p.m.), silicon (0 to 117 p.p.m.) and iron (0 to 50 p.p.m.). Each solution was measured against the appropriate reference solutions containing the single elements at the same concentrations, and the absorbance ratios, A/A° , calculated. The A/A° values were used to calculate interference coefficients, which are a quantitative measure of inter-element interference. With this approach, it is easy to apply corrections to analytical results on unknown solutions.

EXPERIMENTAL

APPARATUS—

Measurements were made with an SP90 atomic-absorption spectrophotometer (Pye-Unicam Ltd.), equipped with a flat-bed chart recorder. The nitrous oxide - acetylene flame was used for silicon and aluminium determinations; the air - acetylene flame was used for determining iron. High spectral output lamps were used for each element. Instrumental conditions are shown in Table I. Polythene apparatus was used to store the solutions.

REAGENTS—

Aluminium solution—Dissolve analytical-reagent grade aluminium sulphate in water to obtain 0.05 per cent. of Al^{3+} .

Iron solution—Dissolve analytical-reagent grade ammonium iron(II) sulphate in water to obtain 0.05 per cent. of Fe^{2+} .

Silicate solution—Dilute with water a sodium silicate solution that has been analysed by a combined gravimetric - colorimetric method. Add a small amount of sulphuric acid

to reduce the pH to a value between 3 and 4. The solution will contain 0.047 per cent. of silicon.

Pyrophosphate solution—Prepare a solution containing 2.0 per cent. of tetrasodium pyrophosphate by dissolving AnalaR grade tetrasodium pyrophosphate in water.

Sodium solution—Dissolve analytical-reagent grade sodium chloride in water to obtain a solution containing 10.0 per cent. of Na^+ .

All solutions were made up with de-ionised water and stored in polythene bottles.

SOLUTIONS—

The respective stock solutions were used to make up a total of 215 solutions representing the single elements (*i.e.*, reference solutions) and the binary and ternary combinations of 0, 20, 40 . . . 100 p.p.m. of aluminium, 0, 23, 47, 70, 94, 117 p.p.m. of silicon and 0, 10, 20 . . . 50 p.p.m. of iron. Each solution (including the reference solutions) also contained tetrasodium pyrophosphate at a concentration equivalent to 7.5×10^{-3} M and added sodium at a concentration of 1.0 per cent. (The sodium addition served to suppress ionisation interference⁷ in the determination of aluminium.) No pH adjustment was made to any of the solutions. On standing, a precipitate formed in some of the solutions; the nature of this precipitate was not investigated and the problem, when it occurred, was avoided by using freshly made solutions. As before, de-ionised water was used throughout and all solutions were stored in polythene bottles.

TABLE I
INSTRUMENTAL CONDITIONS FOR ALUMINIUM, SILICON AND IRON

Element	Wave-length, nm	Slit width, mm	Acetylene flow-rate, l minute ⁻¹	Oxidant flow-rate, l minute ⁻¹	Burner height, mm	Lamp current, mA
Aluminium ..	309.3	0.10	3.8	Nitrous oxide, 5.0	3	10
Silicon	251.6	0.10	4.5	Nitrous oxide, 5.0	10	15
Iron	248.3	0.10	1.0	Air, 5.0	9	15

PROCEDURE—

In studying inter-element interference in the determination of, say, aluminium, a reference solution containing aluminium at a particular concentration was first aspirated into the flame and the absorption recorded. A solution containing aluminium at the same concentration but with silicon and iron now present was then analysed. Absorbances were calculated and the result expressed as the ratio A/A° , where A refers to the solution proper and A° to the reference solution. The same procedure was used for each element at the various concentrations represented in the solutions.

Instrumental base-line settings were made with de-ionised water as the blank solution containing tetrasodium pyrophosphate and added sodium chloride (7.5×10^{-3} M and 1 per cent., respectively) showed negligible absorbance when examined for aluminium, silicon and iron.

RESULTS

The values for the reference solutions, when plotted as absorbance *versus* concentration, gave straight lines for aluminium and silicon, each passing through the origin. A curved plot was obtained with iron (Fig. 1). The remaining results, comprising 495 values of A/A° , were treated in the manner described below.

Consider a solution containing elements 1, 2 and 3 (aluminium, silicon and iron, respectively) at concentrations x_1 , x_2 and x_3 , respectively. Let the measured absorbances at defined resonance lines be A_1 , A_2 and A_3 , respectively. Consider three reference solutions containing the same elements 1, 2 and 3, and at the same concentrations x_1 , x_2 and x_3 , respectively, let the measured absorbances be A_1° , A_2° and A_3° for the same instrument settings.

For the aluminium and silicon reference solutions, absorbance was proportional to concentration over the ranges of interest so that

$$A_1^0 = \alpha_1 x_1 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

$$\text{and } A_2^0 = \alpha_2 x_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

where α_1 and α_2 are absorptivities. (Aluminium and silicon are identified as components 1 and 2, respectively.)

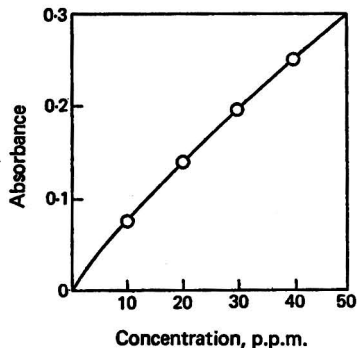


Fig. 1. Plot of absorbance *versus* concentrations for iron

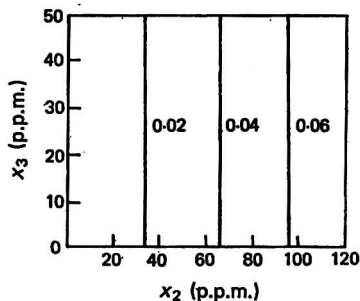


Fig. 2. Inter-element interference in the determination of aluminium. Values of f_1 are shown

For a solution containing all three species we write

$$A_1 = \alpha_1 (1 + b_1 x_2 + c_1 x_3) x_1 \quad \dots \quad \dots \quad \dots \quad (3)$$

$$\text{and } A_2 = \alpha_2 (a_2 x_1 + 1 + c_2 x_3) x_2 \quad \dots \quad \dots \quad \dots \quad (4).$$

In physical terms we assume that in, say, the determination of aluminium in the presence of silicon and of iron, the absorptivity is linearly related to the concentrations of silicon and iron. Here, the various quantities a , b and c , termed interference coefficients, are assumed to be constants. Combining the above, we obtain—

$$\frac{A_1}{A_1^0} = 1 + b_1 x_2 + c_1 x_3 \quad \dots \quad \dots \quad \dots \quad (5)$$

$$\text{and } \frac{A_2}{A_2^0} = a_2 x_1 + 1 + c_2 x_3 \quad \dots \quad \dots \quad \dots \quad (6).$$

For the iron reference solutions, absorbance is not proportional to concentration [*cf.* equation (1)]; the iron curve in Fig. 1 could, however, be described by the relationship

$$A_3^0 = \alpha_3 (1 + K x_3) x_3 \quad \dots \quad \dots \quad \dots \quad (7)$$

with K , in the present work, equal to -0.0061 (p.p.m.)⁻¹. The term in x_3^2 , which is always negative, is negligible when x_3 is small. For the solution containing all three elements we write

$$A_3 = \alpha_3 (a_3 x_1 + b_3 x_2 + 1) (1 + K x_3) x_3 \quad \dots \quad \dots \quad \dots \quad (8)$$

so that

$$\frac{A_3}{A_3^0} = a_3 x_1 + b_3 x_2 + 1 \quad \dots \quad \dots \quad \dots \quad (9).$$

The interference coefficients b_1 and c_1 for aluminium, a_2 and c_2 for silicon and a_3 and b_3 for iron were calculated by regression analysis of each set of 165 A/A^0 values. The results are shown in Table II, together with residual variances and correlation coefficients.

TABLE II
COMPUTER FIT OF ANALYTICAL RESULTS GIVING INTERFERENCE COEFFICIENTS

Determination of stated element	Interference coefficients, p.p.m. ⁻¹			Residual variance	Correlation coefficient
	Al, $a \times 10^4$	Si, $b \times 10^4$	Fe, $c \times 10^4$		
Al	—	-5.89	0.00	0.176	0.872
Si	+1.54	—	+7.38	0.944	0.464
Fe	-3.89	-8.12	—	0.569	0.866

The fit, as judged by the magnitudes of the correlation coefficients, is considered acceptable, therefore justifying the assumed relationships (3), (4) and (9).

DISCUSSION

ANALYSIS OF AN UNKNOWN SOLUTION—

In the analysis of an unknown solution containing all three elements, the values of x_1 , x_2 and x_3 can, in principle, be calculated from the experimental values of A_1 , A_2 and A_3 by solving the set of equations (3), (4) and (8). This tedious procedure can be avoided by defining approximate concentrations y_1 , y_2 and y_3 as—

$$A_1 = \alpha_1 y_1 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

$$A_2 = \alpha_2 y_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (11)$$

$$\text{and } A_3 = \alpha_3 y_3 (1 + Ky_3) \quad \dots \quad \dots \quad \dots \quad \dots \quad (12).$$

They are read off from the calibration curves for the individual elements and represent the values that x_1 , x_2 and x_3 would take on in the absence of inter-element interference. Combining equations (10), (11) and (12) with equations (3), (4) and (8), respectively, gives the approximate relationships—

$$x_1 \sim \frac{y_1}{1 + b_1 y_2 + c_1 y_3} \quad \dots \quad \dots \quad \dots \quad \dots \quad (13)$$

$$x_2 \sim \frac{y_2}{a_2 y_1 + 1 + c_2 y_3} \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

$$\text{and } x_3 (1 + Kx_3) \sim \frac{y_3 (1 + Ky_3)}{a_3 y_1 + b_3 y_2 + 1} \quad \dots \quad \dots \quad \dots \quad \dots \quad (15).$$

To illustrate the calculation, consider the analysis of a hypothetical solution containing 100, 117 and 50 p.p.m. of aluminium, silicon and iron, respectively, these being the maximum concentrations examined here. From the measured absorbances, values of 93.1, 123.1 and 39.7 p.p.m. are read off from the calibration curves for y_1 , y_2 and y_3 , respectively. Insertion in the approximate relationships (13), (14) and (15) gives 100.4, 118.0 and 50.2 p.p.m. as values for x_1 , x_2 and x_3 . As these agree with the chosen values to within 1 per cent., the use of the above approximate relationships in applying the correction factors is considered acceptable. This is a general conclusion.

MAGNITUDES OF THE INTERFERENCES—

The magnitudes of the inter-element interferences can best be judged by defining correction factors f_1 , f_2 and f_3 as follows:

$$x_1 = y_1 (1 + f_1) \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (16)$$

$$x_2 = y_2 (1 + f_2) \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (17)$$

$$x_3 = y_3 (1 + f_3) \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (18).$$

It follows from the data in Table II that f_1 and f_3 are always positive, while f_2 is always negative. The variation of f_1 with x_2 and x_3 is shown in Fig. 2; analogous plots for f_2 and for f_3 are shown in Figs. 3 and 4, respectively. The curves for iron in Fig. 4 have been calculated with $x_3 = 25$ p.p.m.: f_3 is dependent on x_3 because iron does not give a linear calibration curve (Fig. 1).

In the determination of aluminium, silicate has a depressive effect: f_1 becomes +0.07 in the presence of 117 p.p.m. of silicon (Fig. 2). This is consistent with the work of Roos and Price,² with the qualification that these workers found the effect to operate only if a third element such as calcium was present. Iron, at the concentrations used here (50 p.p.m. maximum), does not interfere; a result that is consistent with published work.³

In the determination of silicon, both aluminium and iron, either separately or in combination, enhance the absorption. At the maximum concentrations of 100 and 50 p.p.m. for aluminium and iron, respectively, f_2 was -0.05 (Fig. 3). Again there is agreement with the work of Price and Roos,¹ who investigated the effects of aluminium and of iron on silicate determination. It is curious that while silicon has a depressive effect in the determination of aluminium, aluminium has an enhancing effect in the determination of silicon. It has

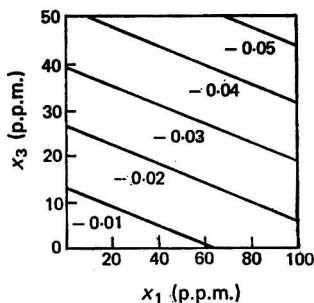


Fig. 3. Inter-element interference in the determination of silicon. Values of f_2 are shown

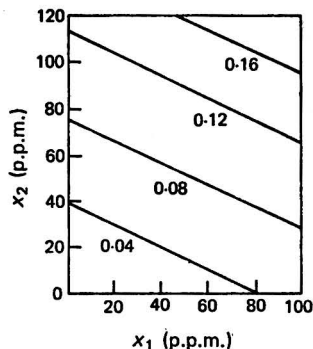


Fig. 4. Inter-element interference in the determination of iron. Values of f_3 are calculated with x_3 equal to 25 p.p.m.

been suggested¹ that both aluminium and iron enhance the absorption of silicon by suppressing the ionisation of silicon atoms in the flame. This explanation is unlikely to apply in the present work because of the high sodium concentration (10^4 p.p.m.). Firstly, such a concentration effectively suppresses ionisation of aluminium⁷ (ionisation potential, 5.98 eV) and should certainly suppress ionisation of silicon (ionisation potential, 8.15 eV). Secondly, iron is present in only small concentrations and its ionisation potential (7.89 eV) is comparable with that of silicon. The problem is thus still unresolved.

In the determination of iron, both silicon and aluminium have a powerful depressive effect. The relative interference ($1 + f_3$) increases with increasing iron concentration. With a true iron concentration (x_3) of 25 p.p.m. and with aluminium and silicon at concentrations of 100 and 93 p.p.m., f_3 is 0.16. This necessitates a large correction and we prefer to work at f_3 values below 0.1 by diluting when necessary. This interference presumably results from the formation of refractory compounds⁶ such as phosphates, silicates and mixed oxides in the cooler acetylene - air flame. (The measurement with binary solutions in which silicate was absent illustrated the depressive effect of aluminium on iron.)

A limited number of further experiments was made to investigate the effect of variations in pyrophosphate concentration (from 3.8×10^{-3} M to 11.3×10^{-3} M) on inter-element interference. The results, when treated by analysis of variance, showed that variations in pyrophosphate concentration between these limits had no significant effect on absorbance ratios for aluminium and silicon. For iron, the effect of increasing phosphate concentration was to depress the absorbance, but the results were insufficient to establish a quantitative relationship.

Finally, the approach used here to express inter-element interference should find application to other interference problems in atomic-absorption spectrophotometry. For the elements of interest here, the use of other instruments, lamps and burners may well lead to small changes in the magnitudes of the interference coefficients. The general conclusions with regard to signs and rough magnitudes should, however, remain unchanged.

We are grateful to Mr. D. Coggon who carried out the computer fitting of the results.

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Non-aqueous Atomic-absorption Spectrophotometric Determination of Organometallic Biocides

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Absorbance results obtained by non-aqueous atomic-absorption spectrophotometry for organotin and organolead biocides have provided calibration graphs that permit quantitative determination of these substances. In a particular application a method is given for measuring the amount of tributyltin chloride recoverable from that deposited on wool under prescribed conditions.

BECAUSE of their powerful biocidal properties, organometallic compounds of tin and lead are of increasing commercial importance as fungicides, bactericides and insecticides.^{1,2} Maximum biocidal activity has usually, but not always, been found in members of the series R_3MX (R representing alkyl or aryl, M tin or lead and X chloride or acetate). Of particular interest to us was the demonstration³ of larvicidal activity of several trialkyltin compounds towards the textile pests *Tineola bisselliella* (common clothes moth) and *Anthrenus vorax* (carpet beetle). To facilitate study of organotin compounds as possible mothproofing agents we required a method by which they could be rapidly and conveniently determined.

The use of tetraethyl-lead in petrol has been followed by the development of procedures^{4,5,6} for lead determination by direct atomic-absorption spectrophotometry of solutions of tetraethyl-lead in iso-octane. Recently,⁷ a similar technique was used in the determination of a copper co-ordination complex dissolved in ethyl acetate.

The present paper describes some observations on the non-aqueous atomic-absorption spectrophotometric determination of several organotin and organolead biocides and, in particular, shows how this technique can be of use in studying textile insectproofing with organometallic substances.

EXPERIMENTAL

MATERIALS—

The organometallic compounds examined were dimethyltin dichloride (I), trimethyltin acetate (II), tributyltin acetate (III), tributyltin chloride (IV), triphenyltin chloride (V), trimethyl-lead acetate (VI), tributyl-lead acetate (VII), triphenyl-lead acetate (VIII) and triphenyl-lead ethyl sulphide (IX). The tin compounds were kindly provided by the Tin Research Institute, Middlesex, U.K., and the lead compounds by Organisch Chemisch Instituut, TNO, Utrecht. Solid compounds were recrystallised until carbon and hydrogen determinations were within 0.3 per cent. of calculated values. Tributyltin chloride (b.p. 171° to 173° C at 25 mm pressure of mercury, n_D^{20} 1.4995) was obtained from Aldrich Chemical Company. Ethanol (95 per cent.) was used; all other solvents were of analytical-reagent grade. The non-ionic surfactant used, Antarox CO630, was a polyoxyethylated nonylphenol from General Aniline and Film Corporation.

SPECTROPHOTOMETRY—

Atomic-absorption measurements were made with a Techtron atomic-absorption spectrophotometer, Model AA3, fitted with an RCA type IP28 photomultiplier and Techtron stainless-steel burner (10 cm, type AB41) with a 0.5-mm slot. The hollow-cathode lamps were by Atomic Spectral Lamps, Melbourne. Operating conditions are given in Table I.

TABLE I
SPECTROPHOTOMETER OPERATING CONDITIONS

		Tin compounds	Lead compounds
Wavelength, nm	286.33	217.00
Lamp current, mA	6	6
Slit width, μm	50	200
Flame	Fuel-rich acetylene (1.7) - air (18.6)*	Coal gas (2.0) - air (18.6)

Bracketed numbers are gas flow-rates, 1 minute⁻¹.

* Since this work was carried out, it has been pointed out that a lower limit of detection for tin should be achieved with a fuel-rich air - hydrogen flame.

PREPARATION OF CALIBRATION GRAPH—

Samples of each of the organometallic compounds (about 0.1 g for lead derivatives and 0.6 g for tin derivatives) are accurately weighed and transferred into standard flasks (50 ml for lead compounds and 100 ml for tin compounds), then dissolved in and made up to volume with the appropriate solvent. These are used as stock solutions; those on which measurements are made are prepared by suitable dilution of the stock solutions. Each solution is aspirated directly into the flame and the absorbance value recorded.

DEPOSITION AND DETERMINATION OF TRIBUTYLTIN CHLORIDE ON WOOL FABRIC—

An emulsifiable concentrate (10 mg) consisting of tributyltin chloride (50 per cent. w/w) and Antarox CO630 surfactant (50 per cent. w/w) is added to 50 ml of 0.05 M potassium chloride - hydrochloric acid buffer (pH 2.0). The resulting emulsion is heated to 60° C and 1.0 g of wool fabric added. After heating for 20 minutes the fabric is removed and dried in an oven at 60° C for 20 minutes. The fabric is then boiled with 50 ml of chloroform for 20 minutes and the chloroform subsequently removed by evaporation. The residue is dissolved in ethanol (5 ml), and the solution is aspirated directly into the flame and the absorbance recorded.

DISCUSSION

Table II illustrates the effect of solvent on the absorbance observed after aspiration of three non-aqueous solutions of tributyltin chloride. A large solvent effect is apparent; this is consistent with observations in other systems.⁸ Ethanol solutions provided the greatest response and, therefore, ethanol was used to obtain absorbance values for the other organotin compounds. Fig. 1 shows that at concentrations up to 0.6×10^{-2} M the calibration graph is both linear and identical for compounds (I), (II), (III) and (IV). Each of these substances must be converted into atomic vapour with equal efficiency. Triphenyltin chloride(V) was the single exception; its atomic absorption was significantly greater than equimolar solutions of any other organotin derivative studied. In this instance the calibration graph was linear up to concentrations of 0.4×10^{-2} M.

TABLE II
EFFECT OF SOLVENT ON THE ATOMIC ABSORPTION OF TRIBUTYLTIN CHLORIDE

Molar concentration $\times 10^4$	Solvent	15.30	30.70	61.40	92.16
		Absorbance			
Ethanol	0.168	0.328	0.638	0.770
Methanol	0.143	0.272	0.456	0.678
Ethyl acetate	0.036	0.086	0.168	0.280

TABLE III

EFFECT OF SOLVENT ON THE ATOMIC ABSORPTION OF TRIPHENYL-LEAD ACETATE

Molar concentration $\times 10^6$					Absorbance				
Solvent									
Ethanol	0.036	0.108	0.328	0.538	0.770
Chloroform	0.022	0.168	0.409	0.638	0.745
Methanol	0.027	0.092	0.284	0.482	0.699
Acetone	0.022	0.071	0.260	0.409	0.569

Similar effects were observed with the organolead compounds examined. Table III illustrates the effect of solvent on the atomic absorption of triphenyl-lead acetate (VIII); chloroform or ethanol were equally suitable, but again the latter was used to obtain absorbance values for compounds (VI), (VII), (VIII) and (IX). Fig. 2 shows by the close fit of all of the

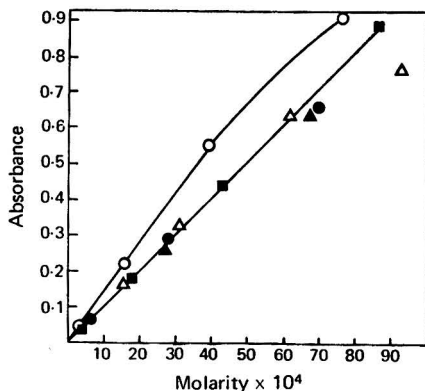


Fig. 1. Calibration graph (ethanol) for organotin compounds: ●, dimethyltin dichloride; ■, tributyltin acetate; ▲, trimethyltin acetate; ○, triphenyltin chloride; and △, tributyltin chloride

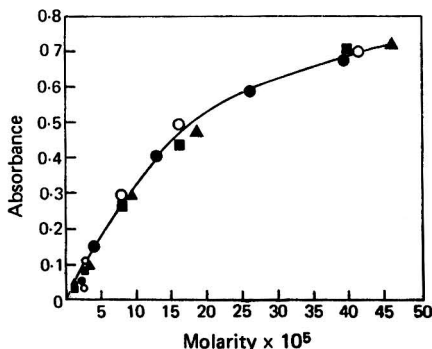


Fig. 2. Calibration graph (ethanol) for organolead compounds: ●, trimethyl-lead acetate; ■, triphenyl-lead ethyl sulphide; ▲, tributyl-lead acetate; and ○, triphenyl-lead acetate

results to a single line that the calibration graphs for all of the organolead compounds are virtually identical at concentrations up to 0.45×10^{-3} M, although linearity was conserved only up to 0.1×10^{-3} M.

Table IV summarises the sensitivities of the atomic-absorption method for determining the organometallic compounds. A limitation is the inherent insensitivity that normally accompanies tin determinations with the conditions described; in this respect the recent report⁹ that organic solvents greatly reduce tin atomic absorbance is of interest. Application of the method to the determination of organotin biocides could result, in some circumstances, in biologically effective doses of the biocide being undetected in the absence of specific efforts to concentrate them. Nevertheless, we have found the atomic-absorption method to be useful in studying textile mothproofing with organometallic compounds. Thus, for example, when tributyltin chloride was adsorbed on to wool from an aqueous emulsion at pH 2.0 to yield a calculated deposit of 0.5 per cent. w/w, only 0.11 per cent. w/w was recovered by extraction of the treated fabric with chloroform. Under standard testing conditions¹⁰ a 0.1 per cent. deposit was found to be the minimum concentration that would mothproof wool (unpublished observation of R. M. Hoskinson and M. Lipson); the treated fabric from which this had been removed by chloroform extraction no longer had a measurable insect resistance, thereby permitting the inference that no significant irreversible adsorption of tributyltin chloride on to wool had occurred.

TABLE IV
SENSITIVITY OF THE ATOMIC-ABSORPTION METHOD IN THE DETERMINATION
OF ORGANOMETALLIC BIOCIDES

Compound	Concentration* required to produce absorbance values of	
	1 per cent.	50 per cent.
I, II, III, IV	1 (12)	49 (590)
V	1 (12)	35 (420)
VI, VII, VIII, IX	0.1 (2)	2 (40)

* The two values given for each absorbance level are molarity ($\times 10^4$) of organometallic compound and micrograms per millilitre of metal (bracketed), respectively.

The possibility exists that some tributyltin chloride will react chemically with the wool protein. Products formed in this way would not be detected by the chloroform extraction procedure.

We thank Mrs. J. Xanthoudakis for expert technical assistance.

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Evaluation of 2-Hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)- 3-naphthoic Acid and Hydroxynaphthol Blue as Metallochromic Indicators in the EDTA Titration of Calcium

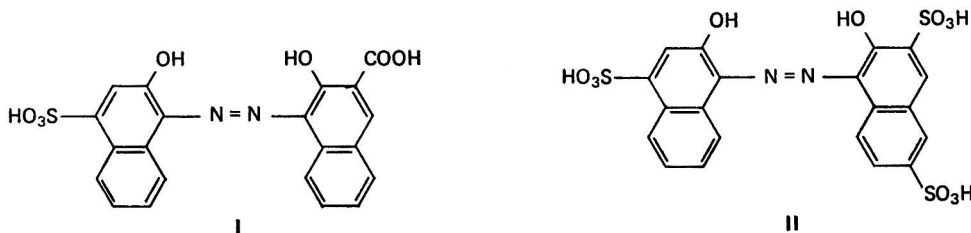
BY ATUKO ITOH AND KEIHEI UENO

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The acid dissociation constants and the chelate stability constants for calcium have been determined spectrophotometrically on purified samples of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Patton and Reeder's dye) (HSN) and hydroxynaphthol blue, both of which have been used as indicators in EDTA titrations of calcium. By comparison of experimental and theoretical curves of the indicator colour change at the end-point, it was found that these two dyes are suitable indicators for the titration of calcium at pH 12 to 13, with a slightly more satisfactory end-point indication given by hydroxynaphthol blue.

SEVERAL metallochromic indicators have been recommended for the EDTA titration of calcium. For instance, Eriochrome black T and calmagite are used at pH 10, phthalein complexone at pH 11 and calcon, 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Patton and Reeder's dye) (HSN), calcein and murexide at pH 12.¹ Of these indicators, HSN and calcon seem to be the most widely adopted for the titration of calcium at higher pH ranges, because sharper end-point colour changes are obtained than with murexide. Recently, a new indicator, hydroxynaphthol blue, has been recommended for use in the method of the United States Pharmacopoeia for the EDTA titration of calcium at pH 12.^{2,3}

Our investigation was undertaken to evaluate HSN (structure I) and hydroxynaphthol blue (structure II) as metallochromic indicators in the EDTA titration of calcium at higher pH ranges, because these two indicators have wider tolerance in these ranges than calcon, which is important in practical applications as precise pH adjustment is not necessary.



After purification of these two indicator dyes, their acid dissociation constants as well as the chelate stability constants of their complexes with calcium were determined photometrically, so that a comparison of the experimental and theoretical curves of the indicator colour change at the end-point could be made. It was found that the two dyes were suitable indicators for the titration of calcium at pH 12 to 13, with a slightly better end-point indication given by hydroxynaphthol blue.

EXPERIMENTAL

PURIFICATION OF INDICATOR DYES—

HSN—Commercial indicator dye (available as Dotite NN pure dye from Dojindo Co., Kumamoto, Japan) (500 mg) was dissolved in 10 ml of hot water containing 20 per cent. of methanol. To this solution, a methanolic solution containing 150 mg of *p*-toluidine was added, and the mixture was heated at 70° C for 40 to 50 minutes. The solution was then allowed to cool to 40° C, when the separated crystals were collected by filtration. Further crystals may be obtained from the filtrate, but this material is not pure enough for use. The first crop was recrystallised from hot water and the pure toluidine salt of the dye was thus obtained as dark violet hygroscopic crystals. The toluidine salt of HSN dye was used throughout these experiments because the amount of toluidine required for its formation did not affect the experimental results.

Analytical results for $C_{21}H_{14}N_2O_7S.C_7H_9N$		C	H	N
Calculated, per cent.	61.64	4.25	7.70
Found, per cent.	61.43	4.42	7.53

Hydroxynaphthol blue—Commercial indicator dye (available as Dotite HNB pure dye from Dojindo Co.) (1 g) was refluxed with 15 ml of ethanol for 1 hour to remove ethanol-soluble impurities. The residue was dissolved in 10 ml of 20 per cent. aqueous methanol solution and the turbid solution centrifuged to obtain a clear dye solution, which was then chromatographed on a cellulose powder column; development was effected with propanol-ethyl acetate-water mixture (5 + 5 + 4). Of the three zones on the column, the lower red zone and the middle zone, which was yellow under ultraviolet light, were rejected. The upper red-violet main zone was eluted and the fraction was concentrated until a precipitate began to appear (about 8 ml). The dye was then precipitated by adding 2 ml of 35 per cent. hydrochloric acid. The pure dye, after separating and drying in a vacuum, consisted of a dark violet hygroscopic powder, which was found to be the monosodium trihydrate salt.

Analytical results for $C_{20}H_{19}N_2S_9O_{14}Na.3H_2O$		C	H	N	Na
Calculated, per cent.	37.74	2.99	4.40	3.65
Found, per cent.	37.86	3.14	4.47	3.42*

* Determined from ash as Na_2SO_4 .

OTHER REAGENTS—

Potassium hydroxide solution, 5, 1 and 0.1 N—Carbonate-free solutions were prepared from analytical-reagent grade potassium hydroxide pellets and de-carbonated water by carrying out the reactions in a nitrogen atmosphere.

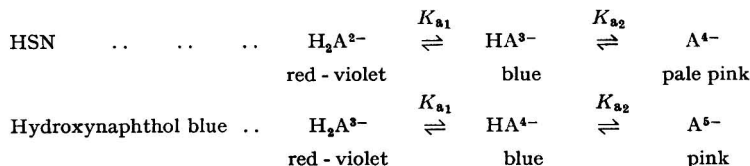
All other reagents were of analytical-reagent grade.

APPARATUS—

pH measurements were made at 24° C with a Hitachi-Horiba, Model P, pH meter. The photometric measurements were carried out with a Hitachi, Model 124, double-beam spectrophotometer and photometric titrations with a Yanagimoto, Model PT-2, photometric titrator.

DETERMINATION OF ACID DISSOCIATION CONSTANTS AND CHELATE STABILITY CONSTANTS OF THE DYES—

The colours of solutions of HSN and hydroxynaphthol blue change with increase in pH according to the following schemes.



These colour changes are understood to be caused by the dissociation of phenolic hydroxyl groups, which are in *ortho*- and *ortho'*-positions relative to the azo group. The absorption

spectra of the predominant ionic species of HSN and hydroxynaphthol blue are shown in Figs. 1 and 2, respectively. Although the spectrum of A^{5-} species of hydroxynaphthol blue could be observed in the higher pH region, as shown in Fig. 2, that of pure A^{4-} species of HSN could hardly be observed even in the higher pH region, which suggested a high pK_2 value for HSN dye. However, the spectrum of A^{4-} species is similar to that of CaA^{2-} , with much lower intensity. As the dissociations of sulphonic acid and carboxylic acid groups occur in the lower pH region, in which these dyes do not function as metallochromic indicators, we determined acid dissociation constants of the last two steps, which correspond to the de-protonation of phenolic groups and occur in the alkaline pH region in which these dyes function as indicators.

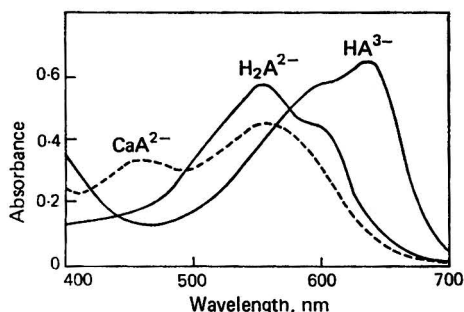


Fig. 1. Absorption spectra of HSN dye and its calcium complex: H_2A^{2-} at pH 3.7; HA^{3-} at pH 9.9; and CaA^{2-} at pH 13. Dye concentration, 2.4×10^{-5} M

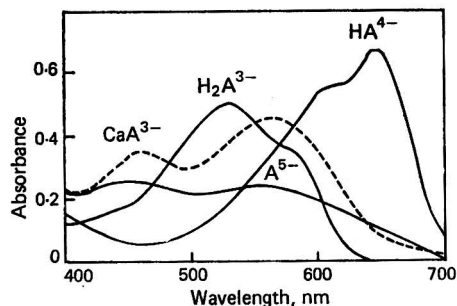


Fig. 2. Absorption spectra of hydroxynaphthol blue dye and its calcium complex: H_2A^{3-} at pH 3.3; HA^{4-} at pH 9.8; A^{5-} at pH 13.8; and CaA^{3-} at pH 13. Dye concentration, 2.4×10^{-5} M

EXPERIMENTAL PROCEDURE FOR THE DETERMINATION OF ACID DISSOCIATION CONSTANTS—

In general, the procedure originally developed by Hildebrand and Reilley⁴ was followed for the determination of acid dissociation and chelate stability constants. Two millilitres of stock dye solution (3.0×10^{-4} M for HSN and 3.13×10^{-4} M for hydroxynaphthol blue) were placed in a thermostatically controlled cell, to which were added, with appropriate amounts of 0.01 M acetic acid, 0.1, 1 or 5 N potassium hydroxide solution to give the desired pH, 0.1 M potassium chloride solution to give an ionic strength (μ) equal to 0.1 and sufficient water to make the volume up to 50 ml. For the solution with pH higher than 11, 1 ml

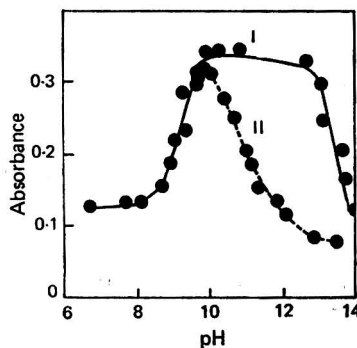


Fig. 3. Absorbance versus pH graph for HSN dye: I, 1.20×10^{-5} M HSN; and II, 1.20×10^{-5} M HSN plus 1.0×10^{-3} M calcium ion. Wavelength, 620 nm

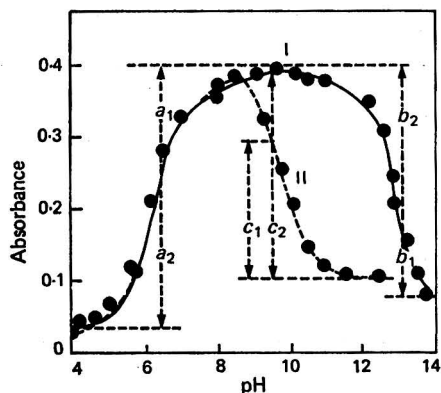


Fig. 4. Absorbance versus pH graph for hydroxynaphthol blue dye: I, 1.25×10^{-5} M hydroxynaphthol blue; and II, 1.25×10^{-5} M hydroxynaphthol blue plus 1.0×10^{-3} M calcium ion. Wavelength, 630 nm

of 2.5 per cent. ascorbic acid was added to prevent the oxidative decolorisation of the dye. For the solution with pH higher than 12.6, the ionic strength of the final solution became greater than 0.1 because of the higher concentration of potassium hydroxide. The pH of the solution was measured after temperature equilibration at 24° C in a nitrogen stream.

After pH measurement, the solution was transferred into an air-tight spectrophotometric cell in a stream of nitrogen, and the absorbance was measured at 620 nm for HSN and 630 nm for hydroxynaphthol blue. The changes in absorbance with pH values are shown in Figs. 3 and 4 for HSN and hydroxynaphthol blue, respectively.

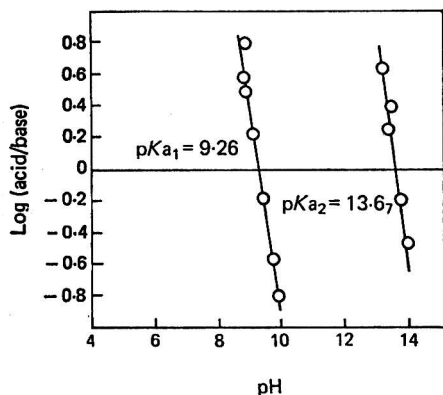


Fig. 5. Log (acid/base) versus pH plot for HSN dye

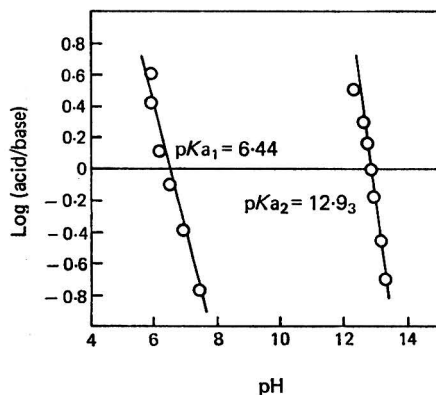


Fig. 6. Log (acid/base) versus pH plot for hydroxynaphthol blue dye

As seen from Figs. 1 and 2, the absorbances at 620 nm for HSN and 630 nm for hydroxynaphthol blue correspond to the concentration of ionic species of HA^{3-} (HSN) and HA^{4-} (hydroxynaphthol blue), respectively. The initial increase in absorbance at these wavelengths indicates de-protonation of the first phenolic group. For example, with hydroxynaphthol blue indicator, as illustrated in Fig. 4, the values of a_1 and a_2 correspond to the concentration of ionic species of H_2A^{3-} and HA^{4-} of hydroxynaphthol blue dye, respectively. Then, in the higher pH region, the decrease in absorbance indicates de-protonation of the last step. With hydroxynaphthol blue, the decrease in absorbance approached nearly to saturation in the higher pH range, which indicated the almost complete de-protonation to A^{5-} species. In this step, the values of b_1 and b_2 in Fig. 4 correspond to the concentration of ionic species of HA^{4-} and A^{5-} of hydroxynaphthol blue. With HSN, however, the absorbance did not approach saturation, even in the higher alkaline range when the pH reading was 13.9. Therefore, the absorbance value, which did not change with further increase of potassium hydroxide, was assumed to be that of A^{4-} species of HSN dye. The value determined with the conditions shown in Fig. 3 was 0.048.

When the values of a_1 and a_2 or b_1 and b_2 at each pH value are substituted in the log(acid/base) term of the following equation,

$$pH = pK_a - \log(\text{acid/base}),$$

the pH when this term equals zero corresponds to the pK_a value. The results are shown in Figs. 5 and 6, and the values are summarised in Table I.

TABLE I
ACID DISSOCIATION CONSTANTS AND CHELATE STABILITY CONSTANTS OF
HSN AND HYDROXYNAPHTHOL BLUE

	HSN	Hydroxynaphthol blue
pK_{a1}	9.26	6.44
pK_{a2}	13.67	12.93
$\log K_{CaA}$	5.85	6.11

$\mu = 0.1$ (KCl) at 24° C.

EXPERIMENTAL PROCEDURE FOR THE DETERMINATION OF CHELATE STABILITY CONSTANTS—

As these two indicators are involved only in the titration of calcium in the higher pH region, the chelate stability constants were determined only for calcium.

Chelate formation by these dyes with calcium ions became most distinct at pH 12 to 13. Accordingly, the ratio of the dye to calcium ion was determined by the continuous variation method at pH 13. The result obtained for HSN dye is shown in Fig. 7. An almost identical curve was also obtained for hydroxynaphthol blue dye. These results show that the ratio between the dye and the calcium ion was 1:1 at pH 13, and also indicate that the dyes are sufficiently pure as the point of maximum absorbance is observed at exactly 0.5 on the abscissa in the continuous variation plots.

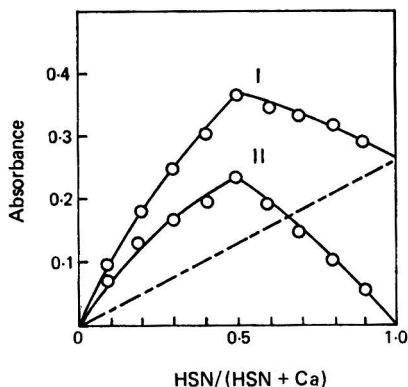


Fig. 7. Continuous variation plots for HSN and calcium; I, absorbance of HSN plus HSN - calcium complex; and II, absorbance related to HSN - calcium complex. Concentration of HSN plus calcium ion, 8×10^{-5} M; wavelength, 460 nm; and pH, 13

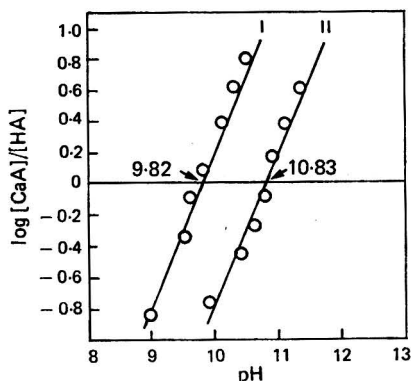


Fig. 8. Log [CaA]/[HA] versus pH plots for HSN and hydroxynaphthol blue dyes: I, 1.0×10^{-3} M calcium ion plus 1.25×10^{-5} M hydroxynaphthol blue dye; and II, 1.0×10^{-3} M calcium ion plus 1.20×10^{-5} M HSN dye

The experimental procedure for the determination of chelate stability constants is essentially the same as that for the acid dissociation constant, except that a 100-fold molar excess of calcium ions was added to the dye solution. Acidic solutions are pink because of the presence of H_2A^{2-} (for HSN) or H_2A^{3-} (for hydroxynaphthol blue). As the pH is increased, the solution becomes blue because of the de-protonation of the first step corresponding to the dissociation constant of K_{a1} . Further increase in pH causes a colour change from blue to pink as a result of calcium - dye complex formation, which intensifies with increasing pH value. The colour change was followed by observing the absorbance of the dye - calcium mixture at 620 nm (HSN) or 630 nm (hydroxynaphthol blue) over a wide pH range. The results are shown in Figs. 3 and 4, respectively.

In these pH ranges, the most important reactions can be expressed as follows.



for which the equilibrium constant is written as

$$K^* = \frac{[CaA][H]}{[Ca][HA]} \dots \dots \dots (1).$$

Therefore

$$pK^* = -\log \frac{[CaA]}{[HA]} + pH + \log [Ca] \dots \dots \dots (2).$$

The first term of the above equation can be correlated with the absorbance results by the following equation—

$$\log \frac{[CaA]}{[HA]} = \log \frac{(C_2 - C_1)}{C_1} \dots \dots \dots (3)$$

where C_1 is the absorbance of the metal plus indicator solution at a given pH value minus the limiting absorbance of this solution in the high pH range and C_2 is the absorbance of the

indicator in the uncomplexed form *minus* the absorbance of the indicator when complexed with calcium ion.

In the presence of excess of calcium ions, a plot of $\log [CaA]/[HA]$ versus pH should yield a straight line with a slope of unity if our assumption is correct. The experimental results obtained for HSN and hydroxynaphthol blue were in good agreement with this prediction, as shown in Fig. 8. The pH value obtained when the first term is equal to zero is substituted in equation (2) and the value for pK^* is then obtained.

Then, the stability constant for the reaction



can be obtained from the following relationship—

$$K = [CaA]/[Ca] \cdot [A] = K^*/K_{a2} \quad \dots \quad (5).$$

The results are summarised in Table I.

PHOTOMETRIC TITRATION OF CALCIUM—

Fifty millilitres of 10^{-3} M calcium solution were titrated photometrically with 0.01 M EDTA solution, with HSN or hydroxynaphthol blue as indicator. A manual photometric titration assembly equipped with a 460-nm filter was used. The titration curves were compared with each other with respect to the sharpness of colour change at the end-point. The theoretical titration curves were also drawn according to Reilley and Schmid,⁶ by using the following equation—

$$a = 1 - [(1 - \phi)/\phi] \cdot 10^{-d_1} + [\phi/(1 - \phi)] \cdot 10^{-d_2} - \frac{C_I/C_M [\phi + 10^{d_1} (1 - \phi)] \cdot 10^{-d_1}}$$

where a is the molar ratio of added EDTA per metal ion; ϕ is the extent of indicator colour change defined by (concentration of uncomplexed dye)/(total dye concentration); d_1 and d_2 are indicator indices, which are defined by $d_1 = \log$ (conditional stability constant of calcium - dye complex) + \log (total calcium-ion concentration) and $d_2 = \log$ (conditional stability constant of calcium - EDTA complex) / \log (conditional stability constant of calcium - dye complex); and finally C_I/C_M is the ratio of indicator and metal-ion concentrations.

The results are summarised in Fig. 9.

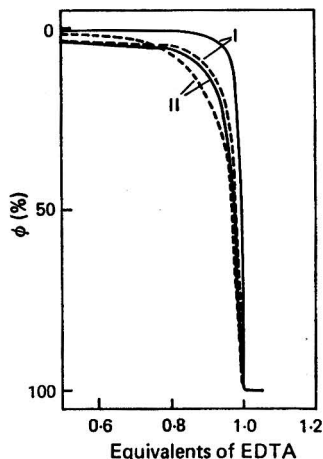


Fig. 9. Colour change for titration of calcium with EDTA, with HSN and hydroxynaphthol blue as indicator: I, theoretical; and II, observed: —, hydroxynaphthol blue; and - - - - -, HSN

STABILITY OF INDICATOR DYES—

Although the metal chelate of HSN indicator dye is fairly stable in alkaline solution, the free dye is unstable and rapidly decolorises. On the other hand, the hydroxynaphthol blue indicator dye, free or complexed, is fairly stable under these conditions. About a 30 per cent. decrease in the absorbance of an aqueous 10^{-5} M dye solution at pH 13 was observed in 5 minutes for free HSN dye, whereas only a 2 per cent. decrease in the absorbance was observed in 20 minutes under the same conditions for free hydroxynaphthol blue dye.

The shelf-life of hydroxynaphthol blue solutions is also longer than that of HSN solutions. The absorbance of aqueous 6.2×10^{-4} M hydroxynaphthol blue solution at room temperature in a dark room was almost unchanged over a period of 60 days.

DISCUSSION

Analytical reagents consisting of azo compounds as supplied by manufacturers are often not pure enough to be used for the determination of physical constants, although they can be used without further purification for general analytical purposes.

Various methods have been tried to purify HSN and hydroxynaphthol blue dyes, however, only those methods described under Experimental gave successful results. There seems to be no general method for the purification of this type of azo dye (*i.e.*, sulphonated *o,o'*-dihydroxy-aromatic azo compounds), and successful methods have to be found by trial and error.

The higher acid dissociation constants of hydroxynaphthol blue dye (lower pK_a value) may result from the inductive effect of three sulphonic acid groups in the molecule compared with one sulphonic acid group in the HSN dye molecule. The values of chelate stability constants of calcium - dye complexes of hydroxynaphthol blue and HSN are higher by about two log units than those of indicators previously reported, such as calcon, Eriochrome black T or murexide. Accordingly, the conditional stability constants for calcium at pH 12 to 13 are the highest of the calcium indicators known so far. With these values and the conditional stability constant of calcium - EDTA chelate, the theoretical colour change curves were drawn, which indicated a very sharp colour change at the equivalence point. The experimental curves before the end-point do not fit well to the theoretical curve, even although they show good end-point breaks. The reasons for the deviation from the theoretical curve may be attributed to the higher potassium-ion concentration (about 0.2 M), the high indicator-to-metal-ion concentration ratio (about 10^{-2})⁵ and the reduced amount of monochromatic light with the filter assembly.

As shown in Fig. 9, both indicators give equally excellent end-point breaks in the photometric titration. However, with visual titrations, the end-point colour change of hydroxynaphthol blue is from wine red to greenish blue, whereas HSN changes from wine red to blue, and the colour change with the former is more easily detectable than that with HSN. These conclusions were also confirmed by titrating calcium in the presence of iron and aluminium (masking with triethanolamine), magnesium or large amounts of sodium chloride.

We are grateful to the Ministry of Education, Japanese Government, for financial aid to cover part of the expenses of this work, and thank Dr. Hiroshi Kobayashi of these laboratories for his valuable advice on the purification of indicator dyes.

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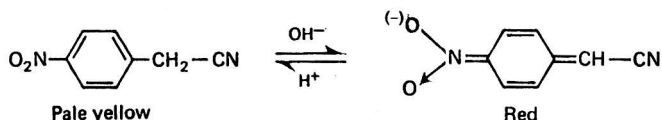
4-Nitrophenylacetonitrile, a Sensitive Reagent for Quinones, Hydroquinone and Pyrocatechol

By L. LÉGRÁDI

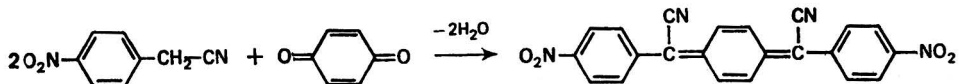
(Nitrokémia Industrial Plants, Fűzfőgyártelep, Hungary)

A new test for quinones, hydroquinone and pyrocatechol is based on the reaction with 4-nitrophenylacetonitrile and alkali.

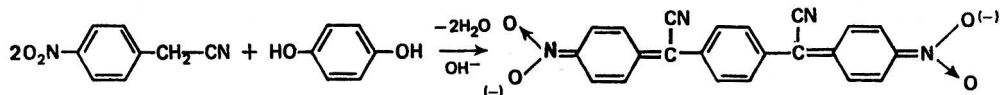
QUINONES give coloured condensation products with rhodamine¹ and with 3-methyl-1-phenylpyrazol-5-one and ammonia.² 4-Nitrophenylacetonitrile has been found to be a sensitive reagent for the detection of quinones, hydroquinone and pyrocatechol. 4-Nitrophenylacetonitrile contains an active methylene group because of the presence of the strong electron attracting cyanide and nitro groups. It behaves as an acid-base indicator.



4-Nitrophenylacetonitrile gives a blue, green or violet colour with quinones, hydroquinone or pyrocatechol and alkali. The same reaction probably takes place as for 3-methyl-1-phenylpyrazol-5-one and quinones.



Hydroquinone behaves in the same way as quinone. If a small amount of hydroquinone and an excess of 4-nitrophenylacetonitrile are used, a blue or green colour is formed, which will be orange or orange-red in acidic solution. Hydroquinone can also form a colour without oxidation.



As the same colour is formed for both quinone and hydroquinone, the hydroquinone is probably oxidised. Phenylacetonitrile also reacts with quinones, hydroquinone and pyrocatechol to yield a green or a blue product, which becomes orange-red in acidic solution, but the reaction is not as sensitive as with 4-nitrophenylacetonitrile. As the reaction also occurs with phenylacetonitrile to yield the same colour as with 4-nitroacetoneitrile, it therefore seems probable, that the nitro group does not play an important rôle in the colour development.

The advantage of 4-nitrophenylacetonitrile reagent over 3-methyl-1-phenylpyrazol-5-one is its more sensitive reaction with quinones and hydroquinone. The limit of identification is not smaller with 4-nitrophenylacetonitrile, as a large excess of this reagent must not be used because of its colour in alkaline medium. 3-Methyl-1-phenylpyrazol-5-one reacts with quinones only in more concentrated solution, whereas the 4-nitrophenylacetonitrile in a greatly diluted solution can also react. For instance, if 1 drop of a 0.2 per cent. ethanolic solution of hydroquinone, 1 drop of a 0.2 per cent. ethanolic solution of 4-nitrophenylacetonitrile and 1 drop of 2 N sodium hydroxide are added to 50 ml of water, a blue colour appears, but no colour is formed with 3-methyl-1-phenylpyrazol-5-one.

EXPERIMENTAL

PREPARATION OF 4-NITROPHENYLACETONITRILE—

A 2.5-ml aliquot of 94 to 98 per cent. nitric acid is added to 2.9 g of phenylacetone and the resulting mixture stirred for 30 minutes while maintaining the temperature below 30° C. The resulting liquid is poured into 50 ml of water and neutralised with alkali. The separated product is filtered and recrystallised from ethanol. The yield is 1.4 g and the melting-point is 116° C (ref. 116° to 117° C).

DETECTION OF QUINONES, HYDROQUINONE OR PYROCATECHOL—

Mix 1 ml of ethanolic test solution, 1 drop of a 0.2 per cent. solution of 4-nitrophenylacetone in ethanol and 1 drop of 0.1 N sodium hydroxide in a test-tube. The mixture is shaken gently. A positive reaction is indicated by the appearance of a green, blue or violet colour. *p*-Benzoquinone and hydroquinone give a green or blue colour and pyrocatechol a violet one depending on the amount of the test substance (over 50 μ g green, below 50 μ g blue). If a large excess of 4-nitrophenylacetone is added to the reaction solution a red colour occurs, which turns green on standing. For a sample of test substance of less than 100 μ g, 0.04 per cent. ethanolic 4-nitrophenylacetone solution must be used. The limit of identification is 0.5 μ g of hydroquinone, 0.5 μ g of 4-benzoquinone, 8 μ g of pyrocatechol and 10 μ g of *o*-benzoquinone.

SPOT TEST FOR QUINONES, HYDROQUINONE AND PYROCATECHOL—

One drop of ethanolic test solution is placed on a filter-paper, followed by 1 drop of 0.2 per cent. ethanolic phenylacetone solution and 1 drop of 0.1 N sodium hydroxide. A positive response is indicated by the appearance of a blue or violet stain edged by a yellow ring. The blank test is red, and the limit of identification is 3 μ g of benzoquinone, 3 μ g of hydroquinone, 30 μ g of pyrocatechol and 30 μ g of *o*-benzoquinone.

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Determination of Water-soluble Sulphate in Acidic Sulphate Soils by Atomic-absorption Spectroscopy

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A method is described for the determination of water-soluble sulphate in soil extracts. After a preliminary conductivity measurement to determine the size of the aliquot to be taken, the sulphate is precipitated by the addition of a known amount of barium chloride. The excess of barium remaining in solution is determined by atomic-absorption spectroscopy and the sulphate content deduced. The method is rapid and compares well with the conventional gravimetric method.

THE oil palm, *Elaeis guineensis* Jacq., grows well on a wide range of soil types, but both growth and yield are severely depressed by the presence of sulphates in excessive amounts. Such excesses have been encountered in the acidic sulphate soil areas, found especially on the west coast of Malaya, where it has been suggested¹ that oil palms should not be planted within 24 inches of the surface in soils with a high sulphate content. The planting programme has produced an urgent need to demarcate areas suitable for planting within the areas where acidic sulphate soils are known to occur. This involves soil surveys and analyses to determine acidity, conductivity and sulphate content. Two of the three criteria used, those of acidity and conductivity, have presented no problems and can be carried out fairly rapidly. However, the determination of water-soluble sulphate at the required speed has raised difficulties.

Little² concluded that the benzidine precipitation method was unreliable, especially for such complex mixtures as soil extracts, and contended that the direct titration of sulphate with barium chloride, with an internal indicator, was simple, rapid and free from serious interference. Middleton³ successfully determined sulphate in plant material by precipitating sulphate with a known amount of barium nitrate and again precipitating the excess of barium with potassium chromate. The remaining potassium chromate was then determined colorimetrically. The gravimetric method has been intensively studied and, although the most commonly used method, it is both slow and tedious. As, on average, 800 samples are tested each week in this laboratory for water-soluble sulphate, the necessity arose to develop a technique that was both rapid and also allowed measurement of the wide range of sulphate contents known to occur in the samples.

EXPERIMENTAL

The method developed, which has been adopted in this laboratory, can be outlined as follows. A known amount of barium chloride is added to an aliquot of the water extract. The excess of barium in solution is then measured by atomic-absorption spectroscopy and the sulphate content deduced. Although the water-soluble sulphate content of acidic sulphate soils can vary between a trace amount and 4 per cent., the whole range can be accommodated by this method, provided appropriate aliquots of soil extracts are taken. Sample size is pre-determined by conductivity measurements. There is good correlation between conductivity and sulphate content, and the former, which is more readily and rapidly determined, is measured first; based on the conductivity value, aliquots are taken for water-soluble sulphate determination. There will, however, be no correlation between conductivity and sulphate content if the soil samples are from very "young" marine clays that are affected by sea water during high tides.

Three methods for sulphate determination were carried out for comparison: (i) gravimetric determination of precipitated barium sulphate, (ii) by using the turbidity technique

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The Use of Paired Ion-sensitive Electrodes to Measure Gradients of pH and of Sodium and Chloride Ions across Actively Transporting Membranes

By D. M. NUTBOURNE*

(Medical Research Council, Department of Experimental Medicine, University of Cambridge)

A method is described in which pairs of ion-sensitive electrodes are used to determine changes in the concentration gradients of pH and of Na^+ and Cl^- ions across an actively transporting membrane. Measurements can be made almost continuously without withdrawing samples. Matched pairs of ion-sensitive electrodes are placed in the membrane chambers with one of each pair on each side of the membrane. A procedure is described by which the potential difference can be measured across these pairs of high-impedance electrodes. The potential difference generated across the transporting membrane is measured independently. From these two sets of values the concentration gradients of H^+ , Na^+ and Cl^- ions across the membrane can be calculated. This method registers gradients of 0.02 pH unit and of 0.5 milli-equivalents l^{-1} of Na^+ and Cl^- ; the changes in ionic concentration can be correlated with the membrane potential almost continuously. Short-circuit current cannot be measured with the electrodes *in situ*. Absolute ionic concentrations in the solutions can be measured at any time by using a standard reference electrode with any of the other electrodes.

THE net rate of active transport of ions across living membranes can be determined from the changes in ionic concentration in the solutions on either side of the membrane. However, when using this method, it is desirable to keep the volume of fluid on each side of the membrane as small as possible, and the withdrawal of samples for analysis may result in the development of small hydrostatic pressure gradients across the membrane. Such gradients may alter the rate of active transport by the membrane.¹

A method is described in which it is possible to monitor almost continuously the concentration gradients of H^+ , Na^+ and Cl^- ions across actively transporting membranes without withdrawing samples. Matched pairs of electrodes sensitive to these ions are left in the solutions, one of each pair on each side of the membrane. The potential difference across each pair of electrodes is a function of the concentration gradient of that ion across the membrane. Absolute concentrations can also be measured intermittently by using a standard reference electrode in conjunction with any of the ion-sensitive electrodes.

METHOD

Various types of Perspex cells for holding the membrane can be used. That used in these experiments is shown in Fig. 1. It consists of a Perspex cell divided by a living membrane into two chambers, each containing Ringer solution. Into the ends of the chambers protrude the potassium chloride - agar leads used in the measurement of potential difference across the living membrane.^{2,3} These leads pass via saturated potassium chloride solution and calomel half-cells to a Vibron electrometer, which measures membrane potential. In the top of each chamber of the cell are five holes, each ground to fit a B7 Quickfit cone. Through these sockets pass the oxygen inlet and outlet and also the H^+ , Na^+ and Cl^- -sensitive

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electrodes (supplied by Electronic Instruments Limited⁴). The H^+ and Cl^- -sensitive electrodes incorporate B7 cones, but the Na^+ -sensitive electrodes are fixed into the cell with rubber washers. The pH and Na^+ -sensitive electrodes are made of special glass and the Cl^- -sensitive electrodes of platinum, coated with silver and chloridised.

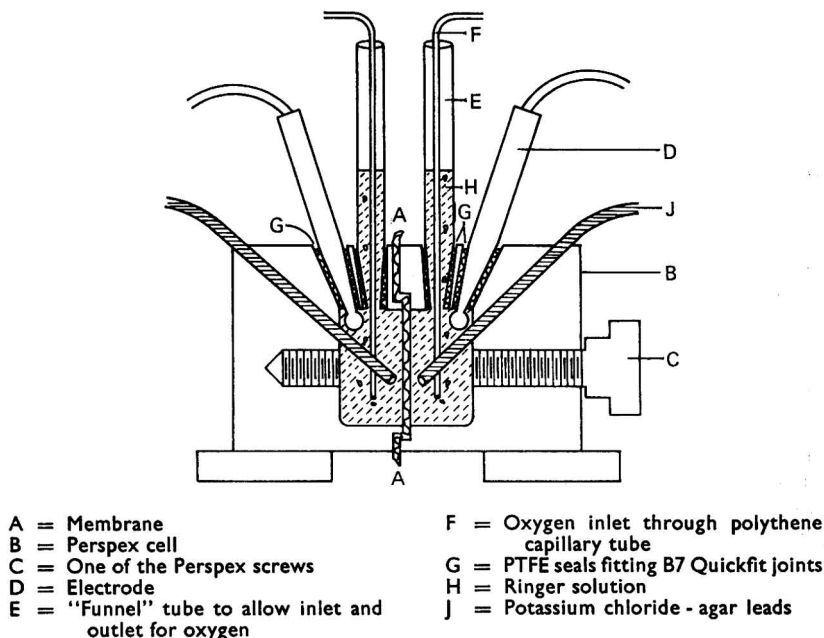


Fig. 1. Diagram of the cell with one pair of electrodes *in situ*

The following account refers only to a pair of pH-sensitive electrodes; the pairs of Na^+ and Cl^- -sensitive electrodes are used in an exactly comparable way. One of each pair of electrodes is connected via a co-axial plug to the high-impedance terminal of the Vibron electrometer; the central core of the co-axial cable of the other electrode is connected to the low-impedance terminal. The screening mesh from the second electrode is connected to the earthed terminal, which is itself joined to the low-impedance terminal. This arrangement is necessary because both electrodes have a high impedance and the electrometer has only one high-impedance input socket.

It has been found necessary to isolate the electrode system from earth; thus, when the cell is placed on the bench no trouble is experienced because the Perspex cell isolates the electrodes from earth. However, when the cell is put into a water-bath, the potential difference measured between the electrodes becomes greater than 1000 mV. The potential difference across the electrodes can again be read accurately when the outside of the cell is kept dry by covering it completely with a thick polythene bag; if either the cell or the polythene bag leaks or condensation occurs so that the outside of the cell becomes wet, then the electrode potential difference immediately rises to above 1000 mV.

STANDARDISATION—

Each matched pair of electrodes is mounted in the cell and connected to the electrometer as described. At first, there is no membrane in the cell so that both electrodes are in the same solution. A series of suitable standard solutions (with pH ranging from 9 to 4 and sodium chloride concentration ranging from 0.05 to 0.3 M and with an ionic background similar to the Ringer solutions) is placed in the cell and the potential difference is measured across each pair of electrodes in each solution. This basic electrode potential difference, $P.D._{electrode}$, varies slightly from one pair of electrodes to another, but it is constant for each individual pair of electrodes.

Next, a piece of cellophane is placed in the cell to act as a semi-permeable membrane between the chambers. Two different standard solutions are introduced one on each side of the membrane and for each combination of solutions the total potential difference, $P.D._{total}$, is measured across the pairs of electrodes. With the pH-sensitive electrodes, a difference of 1 pH unit across the membrane gives a constant potential difference reading across the electrodes at all pH values from 4 to 9; this potential difference lies between 55 and 65 mV per pH unit and is constant for each pair of electrodes. Positive or negative values are obtained, depending on which electrode is in the more acidic solution.

It is, therefore, possible to determine the difference in pH across the membrane by measuring the potential difference generated across the electrodes:

$$\text{Number of millivolts resulting from the pH difference} = (P.D._{total} - P.D._{electrode}).$$

When the electrodes are moved from identical solutions to solutions of dissimilar pH, it is possible not only to measure the difference in pH, but also to ascertain which solution is the more acidic by determining whether the change in millivolts is positive or negative.

LIVING MEMBRANES—

To use this method in the presence of living membranes, a further factor has to be considered, as the electrodes measure not only the potential difference caused by the pH difference but also that generated across the living membrane as a result of active ionic transport, *i.e.*, $P.D._{membrane}$. Therefore, it is necessary to measure the latter by independent means and subtract this value from the total potential difference registered by the electrodes. It is essential when making these measurements that all potential differences should be measured in the same direction, *i.e.*, the electrodes and the potassium chloride - agar lead from the same side of the membrane must be connected to the same terminal of the electrometer. The potential difference values measured, together with their positive or negative signs, can then be used to calculate the pH gradient across the membrane:

$$\text{Potential difference resulting from pH difference} = (P.D._{total} - P.D._{electrode} - P.D._{membrane}).$$

From this, the pH difference can be calculated since the number of millivolts generated for each unit of pH difference between the electrodes has already been determined.

It is not possible to measure the number of millivolts generated by the membrane on one electrometer while simultaneously measuring the potential difference generated across the glass electrodes on a second electrometer, because when the two electrometers are simultaneously connected to one cell, both give full-scale deflections. Therefore, the membrane potential is measured first, and immediately afterwards the electrode potential is measured on the same electrometer.

The sodium and chloride electrodes are standardised and used in the same way, using standard sodium chloride solutions for their calibration.

Absolute concentrations of H^+ , Na^+ and Cl^- ions in the solution can be determined at any time by using a standard reference electrode in conjunction with the appropriate indwelling ion-sensitive electrode. The reference electrode is not left *in situ* because, during a lengthy experiment, the leakage of electrolyte from the electrode would contaminate the Ringer solution. To minimise the changes in pressure in the solutions surrounding the membrane, which might take place when the reference electrode is introduced, and also to minimise contamination, the reference electrode is connected to a bridge system containing Ringer solution and terminating in a capillary tube containing a ceramic plug.⁵ Only the tip of this plug is introduced into the solution.

It is not possible to measure the current flowing across membranes at zero potential during these experiments, because the external voltage applied to nullify the membrane potential⁶ interferes with the electrical responses of the electrodes.

RESULTS

The method described above has been used to observe the changes in concentration of H^+ , Na^+ and Cl^- ions taking place in the solutions surrounding isolated frog-skin and pig chorioallantoic membranes. At the beginning and end of each experiment, the absolute concentrations of H^+ , Na^+ and Cl^- ions were measured in the solutions by using a calomel half-cell reference electrode in conjunction with each of the ion-sensitive electrodes.

In all instances the values for the concentration gradients obtained from the matched pairs of electrodes agreed closely with those obtained by measuring the absolute ionic concentrations in the solutions on the two sides of the membrane. The matched pairs of electrodes registered differences of pH to an accuracy of 0.02 pH unit and differences of Na^+ and Cl^- to an accuracy of 0.5 milli-equivalents l^{-1} .

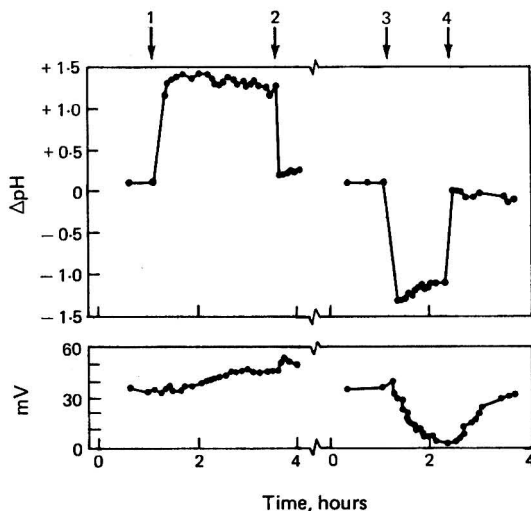


Fig. 2. Demonstration of the use of a pair of pH electrodes to correlate changes in pH gradient across a frog skin with the membrane potential. The Ringer solution contained 103, 1, 1.8 and 94 milli-equivalents l^{-1} of Na^+ , K^+ , Ca^{2+} and Cl^- , respectively, and 20 mg per cent. of inorganic phosphorus as mixed phosphates. Membrane potential measured in millivolts, the inside of the skin being positive in relation to the outside. ΔpH is the pH gradient measured by the glass electrodes across the membrane, positive values indicating lower pH of solution on outside of the skin and negative values lower pH of that on inside. At (1), (2), (3) and (4), solutions were changed on both sides of the membrane; after (1), pH was lower on outside of skin and after (3), lower on inside. After (2) and (4), pH was approximately the same on both sides. pH values of solutions before and after (1), (2), (3) and (4) are shown in Table I

Fig. 2 illustrates one use of this method. It shows the results of an experiment in which the changes in pH gradient across an isolated living frog skin are compared for several hours with changes in the membrane potential without the removal of samples. Using a reference electrode, the absolute pH was measured on each side of the membrane before and after each change of solution. These results are shown in Table I. It can be seen that the difference in the absolute pH values measured in the solutions on each side of the skin correlates closely with the values for the pH gradient obtained by using a pair of glass electrodes.

DISCUSSION

When the physiology of living isolated membranes is being studied it is an advantage to be able to observe their behaviour continuously during an experiment. The method described above, in which matched pairs of electrodes are used, makes it possible to observe

TABLE I
pH VALUES OF THE SOLUTIONS ON EACH SIDE OF A LIVING FROG-SKIN
MEMBRANE IN THE EXPERIMENT SHOWN IN FIG. 2

Solutions tested (Fig. 2)	pH of solution inside skin (pH _i)	pH of solution outside skin (pH _o)	pH _i - pH _o	pH gradient measured by two electrodes (Δ pH)
Before (1)	7.126	7.070	+0.056	+0.080
After (1)	7.123	5.795	+1.328	+1.320
Before (2)	7.088	5.799	+1.289	+1.290
After (2)	7.125	6.954	+0.171	+0.190
Before (3)	7.191	7.113	+0.078	+0.100
After (3)	5.820	7.136	-1.316	-1.320
Before (4)	6.028	7.124	-1.096	-1.110
After (4)	7.112	7.124	-0.012	-0.002

almost continuously the changes in concentration of H⁺, Na⁺ and Cl⁻ ions in the solutions on opposite sides of living membranes. This method has the advantage that concentration gradients across membranes can be followed almost continuously without the necessity of withdrawing samples, and in this way the volumes and pressures of the solution surrounding the membrane are kept constant. Valuable information on membrane behaviour can be obtained by correlating the changes in the concentration gradients of H⁺, Na⁺ and Cl⁻ ions across the membranes with the changes in membrane potential.

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A Simple Colorimetric Method for the Determination of Iron in Serum

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Iron in serum is freed from its attachment to protein with hydrochloric acid and the proteins are precipitated with trichloroacetic acid. A coloured complex is formed with metamizol in the presence of a high concentration of hydrogen peroxide, the absorption maximum at 440 nm being used for its colorimetric determination. The complex is relatively stable and its absorption obeys Beer - Lambert's law up to 400 μg of iron per 100 ml. Recovery experiments and comparison of a series of determinations with a widely used colorimetric method showed no statistical difference from expected values.

ALMOST all of the methods available for determining serum iron involve splitting and isolating the iron from its combination with the iron-binding globulin. Acids, reducing agents, heat or quadrivalent thorium¹ are used alone or combined to prevent the precipitation of iron with the proteins.

Methods used for the development of a colour with iron include the use of thiocyanate,^{2,3} ferricyanide,⁴ 2,2'-bipyridyl,^{5,6,7,8,9} *o*-tolidine,¹⁰ 1,10-phenanthroline,¹¹ bathophenanthroline,¹² the water-soluble sulphonated derivative of bathophenanthroline¹³ or terpyridyl.¹⁴

Metamizol, sodium 1-phenyl-2,3-dimethyl-3-pyrazolone-5-one-4-methylaminomethane-sulphonate, used in the present method, is a common analgesic drug (trade name Novalgine, Hoechst). When treated with hydrogen peroxide, it forms a blue colour, which fades fairly rapidly, followed by a reddish yellow colour caused by the formation of rubazonic acid [1-phenyl-4-(1-phenyl-5-oxo-3-methylpyrazolinylidene-4-amino)-3-methylpyrazolone].¹⁵ It was observed that in the presence of iron the colour is greatly intensified and is proportional to the amount of iron present. The most probable tentative explanation of the reaction is that the reddish compound (rubazonic acid) formed reacts with iron to form a coloured "iron - rubazonic acid complex," which has a molar extinction coefficient much greater than that of rubazonic acid.

The coloured complex is best formed when the standard iron solution is already mixed with the metamizol solution at the time of addition of the hydrogen peroxide, as indicated in the following experiment in which metamizol and hydrogen peroxide solutions were mixed and the standard mixture (iron solution *plus* hydrochloric acid *plus* trichloroacetic acid) was added at different intervals, the reading being carried out after a period of 20 minutes.

Time of addition of the standard iron solution after mixing metamizol and hydrogen peroxide solutions, minutes ..	0	5	10	15	20	25	30
Net optical density* (standard reading—reagent blank reading)	0.225	0.160	0.140	0.120	0.095	0.090	0.090

* Standard iron equivalent to 200 μg per 100 ml.

As seen above, the extinction of the mixture was at a maximum when the standard iron solution was added at zero time.

Rubazonic acid cannot easily be obtained and in this paper a simple sensitive method is described in which use is made of a readily available reagent. The iron content in the serum is thus determined by its colour reaction with metamizol in the presence of hydrogen peroxide, the yellowish orange complex being formed at a pH value of 0.9.

METHOD

Glassware is kept overnight in 50 per cent. hydrochloric acid and then thoroughly washed with de-ionised water.

REAGENTS—

All reagents must be of analytical-reagent grade and de-ionised water is used throughout. *Hydrochloric acid*, 10 per cent. *v/v*—Dilute 100 ml of concentrated hydrochloric acid (sp.gr. 1.18) to 1 litre.

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Trichloroacetic acid, 30 per cent. w/v—Dissolve 30 g of trichloroacetic acid in de-ionised water and make the volume up to 100 ml.

Metamizol, 20 per cent. w/v—Dissolve 2 g of metamizol in 10 ml of de-ionised water. The solution must be freshly prepared just before use.

Hydrogen peroxide, 100 volume, B.P.—Keep the solution in a refrigerator at 4° C in a glass-stoppered dark bottle.

Stock standard iron solution, 5 mg ml⁻¹ of iron—Dissolve 4.31 g of ammonium iron(III) sulphate, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, in de-ionised water. Add 10 ml of concentrated hydrochloric acid and make up to 100 ml with de-ionised water. The stock iron standard is standardised by iodimetric titration against standard sodium thiosulphate solution.

Working standard iron solution, 50 µg ml⁻¹ of iron—Dilute 1 ml of the stock standard solution to 100 ml with de-ionised water.

Dilute working standard iron solution, 1 µg ml⁻¹ of iron—Dilute 2 ml of the working standard solution to 100 ml with de-ionised water.

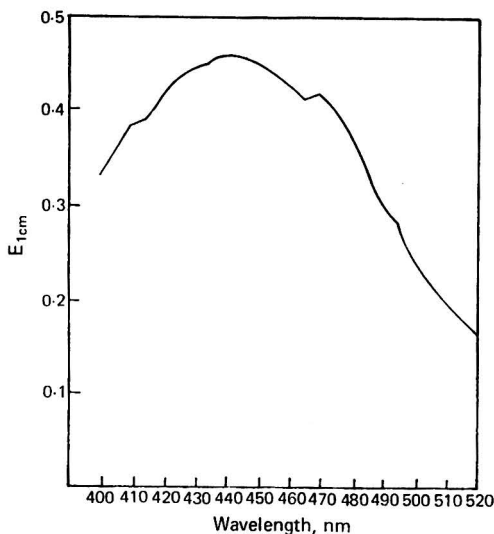


Fig. 1. Absorption graph of the coloured complex

PROCEDURE—

Add 1 ml of serum to 1 ml of de-ionised water in a wide centrifuge tube. Add 1 ml of 10 per cent. hydrochloric acid and set the mixture aside at room temperature for 10 minutes. Then add 0.4 ml of 30 per cent. trichloroacetic acid and stir with a small glass rod for 1 minute.

Allow the mixture to stand again for 10 minutes and centrifuge the tube at 3000 r.p.m., at a mean radius of 15 cm, for 20 minutes. (No change in volume occurs on precipitating the serum proteins in such a concentrated solution.) Carefully remove the supernatant fluid. Introduce 1 ml of the supernatant fluid into a test-tube and add to it 0.3 ml of the 20 per cent. metamizol solution. After 30 s add 3 ml of 100-volume hydrogen peroxide and mix the contents. The solution will be ready for colorimetric examination 20 minutes after the addition of the hydrogen peroxide. The absorption maximum occurs at 440 nm as determined with a quartz spectrophotometer (Fig. 1). Throughout this study, a Unicam SP600 spectrophotometer was used. The instrument is set at zero with de-ionised water, and the optical densities of the reagent blank, standard and test solutions are measured at 1-minute intervals. (The mean blank reading was 0.20 extinction in a 1-cm path, with a maximum of 0.215. As indicated, this value is subtracted from all readings.)

One millilitre of de-ionised water and 1 ml of dilute working standard solution (1 µg ml⁻¹ of iron) are treated in a similar way to the test serum to serve as reagent blank and standard, respectively.

CALCULATION—

Iron per 100 ml of serum, μg

$$= \frac{\text{Optical density of test serum} - \text{optical density of reagent blank}}{\text{Optical density of standard} - \text{optical density of reagent blank}} \times 100.$$

CALIBRATION GRAPH—

From the stock ammonium iron(III) sulphate standard, a dilute working standard was prepared containing $2 \mu\text{g ml}^{-1}$ of iron and used in the preparation of the standard calibration graph as follows.

Iron per 100 ml of serum, μg ..	0	50	100	150	200	250	300	350	400
Dilute working iron standard ($2 \mu\text{g ml}^{-1}$), ml	0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2
De-ionised water, ml	2	1.75	1.5	1.25	1.0	0.75	0.5	0.25	0

Add 1 ml of 10 per cent. hydrochloric acid to each tube and proceed exactly as with the test serum.

The typical calibration graph of serum iron plotted against $E_{1\text{cm}}$ gives a straight line passing through the origin for concentrations of iron up to $400 \mu\text{g}$ of iron per 100 ml of serum, at which concentration $E_{1\text{cm}}$ is 0.47.

EXPERIMENTAL

EFFECT OF TIME—

The stability of the coloured complex was investigated by recording the spectrophotometric readings at intervals of 1 minute after addition of the hydrogen peroxide. During the intervals between 10 and 60 minutes, the readings did not change by more than 1 per cent. Accordingly, the period of 20 minutes was chosen for the working conditions.

EFFECT OF ACIDITY—

Comparable results were obtained when the pH of the final reaction mixture was between 0.5 and 1.4. At pH values above 3 the colour did not develop.

REPRODUCIBILITY—

A specimen of pooled sera was used. Twelve replicate determinations were carried out by the method described, which showed a range of 80 to $90 \mu\text{g}$, with a mean of $85.42 \mu\text{g}$, of iron per 100 ml, the standard deviation being $\pm 3.62 \mu\text{g}$ per 100 ml.

EFFECT OF THE PRESENCE OF METAMIZOL IN A PATIENT'S SERUM—

As metamizol is a commonly used drug, it was necessary to investigate the effect of its presence in the patient's serum on the colour reaction. It was found that in the usual therapeutic doses used metamizol did not produce the coloured complex, which developed satisfactorily only when the concentration of metamizol reached 20 per cent.

In Table I the results obtained with a series of concentrations of metamizol solution ranging between 10 and 20 per cent. are given. The extinction of the reagent blank and of a standard iron solution equivalent to $200 \mu\text{g}$ per 100 ml were recorded.

TABLE I
EXTINCTION

Concentration of metamizol, per cent.	Reagent blank	Iron standard ($200 \mu\text{g}$ per 100 ml)	Net reading (standard reading— blank reading)
10	0.060	0.153	0.093
11	0.073	0.175	0.102
12	0.090	0.203	0.113
13	0.103	0.233	0.130
14	0.116	0.257	0.140
15	0.131	0.282	0.151
16	0.143	0.310	0.167
17	0.154	0.337	0.183
18	0.173	0.370	0.197
19	0.190	0.394	0.204
20	0.205	0.425	0.220

All readings are the mean of duplicate determinations.

As seen from Table I, the extinctions of the reagent blank and the iron standard, as well as the net readings, are maximal with a concentration of 20 per cent. of metamizol solution, and also lie within the most satisfactory range for photoelectric measurements between 0.2 and 0.7, hence the recommended use of a 20 per cent. solution.

EFFECT OF METAL IONS—

Copper, zinc, cobalt and lead ions used alone, or incorporated with the ammonium iron(III) sulphate stock standard solution, in amounts equivalent to 5 mg of metal per 100 ml had no effect on the colour reaction.

RECOVERY OF ADDED IRON—

The initial iron concentrations of ten 15-ml samples of serum were established by duplicate determinations. Then 0.2, 0.4, 0.6, 0.8 and 1.0 ml of a 200 μg per 100 ml standard iron solution were added to 1-ml portions of each serum and the volume made up to 2 ml

TABLE II

RECOVERY OF IRON ADDED (μg PER 100 ml) TO SERUM AS AMMONIUM IRON(III) SULPHATE

Specimen No.	1.0		1.0		1.0		1.0		1.0		
	Found	Ex-pected	Found	Ex-pected	Found	Ex-pected	Found	Ex-pected	Found	Ex-pected	
1	45	90	85	116	125	168	165	200	205	238	245
2	66	104	106	138	146	185	186	230	226	250	266
3	62	110	102	138	142	190	182	224	222	256	262
4	85	117	125	166	165	200	205	238	245	280	285
5	112	156	152	200	192	230	232	280	272	300	312
6	92	138	132	172	172	220	212	250	252	284	292
7	117	156	157	190	197	246	237	280	277	309	317
8	97	138	137	168	177	218	217	247	257	300	297
9	56	100	96	132	136	176	176	224	216	260	256
10	62	100	102	147	142	174	182	230	222	250	262

TABLE III

COMPARISON OF PRESENT METHOD WITH THAT OF MARRACK

Serum sample	Iron content, μg per 100 ml, by—		Serum sample	Iron content, μg per 100 ml, by—	
	Present method	Marrack's method		Present method	Marrack's method
1	101	98	23	160	162
2	66	64	24	102	100
3	93	93	25	68	70
4	135	130	26	142	146
5	184	180	27	98	102
6	77	72	28	84	82
7	113	117	29	149	149
8	136	134	30	79	77
9	86	82	31	100	102
10	54	56	32	82	82
11	99	102	33	86	85
12	122	120	34	173	172
13	64	65	35	165	169
14	102	100	36	90	91
15	69	67	37	84	82
16	138	137	38	59	57
17	200	196	39	198	204
18	176	182	40	137	134
19	156	151			
20	92	91	Mean ..	113.6	113
21	114	112	\pm S.E...	6.33	6.48
22	107	105			

with de-ionised water (giving a concentration of 40, 80, 120, 160 and 200 μg of iron per 100 ml above the initial concentration). The results of the recovery experiment (each is a mean of duplicate determinations) are shown in Table II. Statistical analysis of the difference between expected and determined values for serum iron after adding various amounts of iron to the serum samples showed no significant difference ($t = 0.09$ and $P > 0.9$).

COMPARISON WITH MARRACK'S METHOD⁹—

Forty samples of venous blood covering a range of 54 to 200 μg of iron per 100 ml of serum were taken from forty patients chosen at random. Determinations in duplicate were made on each serum sample by both the proposed method and Marrack's method. Table III shows the mean of the duplicate results by both methods. No statistical difference was noted between the two methods ($t = 0.0447$ and $P > 0.9$).

CONCLUSION

The proposed method can be recommended for the determination of iron in serum. It has the advantage over existing chemical methods of being more economical of serum, and that all reagents used are available and cheap. Moreover, in most other methods the iron has to be maintained in the reduced state to give the colour reaction but this is not necessary in the present method. The stability of the colour is also high without undue complication of the working procedure. Further, the colour reaction is carried out in a strongly acidic medium, while in many of the other methods neutralisation of the solution is required as a preliminary to colour development.

We thank Dr. Sedki A. Khair of the Department of Physiology for the statistical analysis of the results.

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Book Reviews

QUANTITATIVE ANALYTICAL CHEMISTRY. VOLUME I. INTRODUCTION TO PRINCIPLES. By H. A. FLASCHKA, A. J. BARNARD, JUN., and P. E. STURROCK. Pp. xiv + 592. New York: Barnes & Noble, Inc. 1969. Price \$5.95.

QUANTITATIVE ANALYTICAL CHEMISTRY. VOLUME II. SHORT INTRODUCTION TO PRACTICE. By H. A. FLASCHKA, A. J. BARNARD, JUN., and P. E. STURROCK. Pp. x + 290. New York: Barnes & Noble, Inc. 1969. Price \$2.95.

Most elementary texts on analytical chemistry have a familiar format. The law of mass action is discussed, and its implication in acid - base titrations, precipitation, complexing and redox reactions is developed. The present text is no exception, and is as informative on this topic as many other similar books for first-year university students. In addition, however, discussions of most of the important instrumental methods and more advanced processes of analysis are included, and a second volume is required to give a detailed account of analytical technique and practical exercises.

It must be mentioned that many of the instrumental and allied chapters are little more than summaries, and as such are not likely to contribute much knowledge to the student. The authors will argue that a more detailed treatment is outside the bounds of a first-year undergraduate course, but it would have been helpful, for example, if a reasonable discussion of the uses of atomic absorption or X-ray fluorescence had been given. And this argument certainly cannot apply to the section on carbon, hydrogen and nitrogen analysis, which is content to inform the reader that H_2O is absorbed by "a water absorbing material," and CO_2 is absorbed in an "absorption tube for CO_2 ." The inclusion of important instrumental methods in such a brief and vague manner belittles their importance in comparison with the more classical methods of analysis. For example, 7 pages are devoted to solvent extraction, 10 to all types of chromatography and more than 120 to aspects of acid - base equilibria!

There are several pleasing features of the text. Most important, its price is low enough for it to be bought by those for whom it is intended. The use of a separate volume for the practical side will keep the larger theory volume in better condition (but hopefully not from lack of use). Amongst the individual chapters, the treatment of complexometric titrations is very clear, and the natural development of electrochemical processes from redox titrations to polarography is also good. Topics such as masking and formal potential, often missing from competitive texts, are also included, but a chapter on organic reagents would have been a welcome addition.

Another deficiency of both volumes is a lack of indication of current usage of the general methods described. When are particular redox titrations used these days? Is polarography widely used in the determination of metals, or has atomic absorption or X-ray fluorescence displaced it? At the very least a list of standard texts for further reading should have been included. In many ways, the text reads like a lecture course. It has a wordy, conversational style (not favoured by the reviewer), and one can imagine students reading the book *in lieu* of listening to a lecturer, rather than for expanding the notes taken at a lecture. Finally, there is a tendency to dwell on older usage at the expense of modern technique, the equal-arm balance is treated at greater length than the one-pan balance; a glass wash bottle is accorded pride of place over a plastic one; classical methods of gas analysis are treated in 5 pages, whereas the use of various physical and chromatographic techniques is disposed of in 5 lines.

ALAN TOWNSEND

COMPUTERS AT WORK. Edited by JOHN O. E. CLARKE, B.Sc., A.R.I.C. Pp. 160. London, New York, Sydney and Toronto: The Hamlyn Publishing Group Ltd. 1969. Price 6s.

MATHEMATICS. By CHARLES SOLOMON. Pp. 160. London, New York, Sydney and Toronto: The Hamlyn Publishing Group Ltd. 1969. Price 6s.

These two little paperbacks are separately very interesting and readable, their illustrations are clear and to the point. Mathematics touches on the practical in probabilities, and on the theory in infinite series. Computers gives the reader a broad ranging realistic view of several of the applications to which computers are being put today, in addition to indicating some interesting future developments.

P. L. EVANS

THE USE OF CHEMICAL LITERATURE. Edited by R. T. BOTTLE. Second Edition. Pp. xii + 294. London: Butterworth & Co. 1969. Price 65s.

The chemist cannot afford to mis-use the chemical literature. Measured in terms of the man-years taken to produce it, the chemical literature is the most expensive tool available to him. About four million papers, reports, patents, etc., have been published and this number is doubling approximately every 10 years or so. The editor of this volume calculates that if plausible estimates are made for the number of man-hours each item of the chemical literature represents to produce and store, and if this is costed at current levels, the literature probably represents £10¹⁰ to £10¹¹ worth of chemical research already completed. We are thus already surrounded by a vast ocean of chemical literature. If a new graduate surveys this ocean at the start of his career he can be reasonably certain, even with a relatively conservative figure for the growth rate, that its volume will have increased by one order of magnitude by the time he retires. It is, therefore, essential that the chemist gains a working knowledge of the literature and the most efficient ways of utilising it for his own purposes.

This book marks the formal start of a new series of literature guides entitled Information Sources for Research and Development, under the general editorship of D. J. Foskett and R. T. Bottle. The first edition of this text, however, was published in 1962. It has been almost completely rewritten and only two chapters remain substantially the same. The volume contains seventeen chapters contributed by thirteen authors. Several general chapters are concerned with libraries and their use, abstracts and information retrieval, translations and their sources (with special reference to Russian literature), the use of patent literature and a guide to government and trade publications of interest to the chemist. Specific chapters are devoted to the literature of inorganic chemistry, nuclear chemistry and polymer science and the use of Standard Tables of Physical Data and Beilstein's *Handbuch*. Additional chapters deal with some less conventional methods of obtaining information, the history and biography of chemistry and the practical use of the chemical literature. Appendices contain a brief glossary of some abbreviations, acronyms and miscellaneous useful terms and also suggestions for practical work. The stated aims of the book are not to make every bench chemist his own technical librarian, but to save him and his library colleagues time and enable him to use to the full the excellent library facilities that are within the reach of all. The present reviewer found the book somewhat disjointed; it seems that this topic may not lend itself readily to a multiplicity of authors. Analytical chemistry receives short but adequate treatment in the chapters on inorganic and organic chemical literature. This volume should prove to be a most useful guide for students and will be of general interest to all practising chemists. It will be bought by technical libraries but probably not by individuals. G. F. KIRKBRIGHT

INTERNATIONAL COMPENDIUM OF NUMERICAL DATA PROJECTS. A SURVEY AND ANALYSIS. Produced by CODATA, THE COMMITTEE ON DATA FOR SCIENCE AND TECHNOLOGY OF THE INTERNATIONAL COUNCIL OF SCIENTIFIC UNIONS. Pp. xxiv + 295. Berlin, Heidelberg and New York: Springer-Verlag. 1969. Price DM 48.

The Committee on Data for Science and Technology (CODATA) was set up by the International Council of Scientific Unions in 1966 to promote collections of critically selected numerical data. This book is the outcome of the initial task assigned to CODATA, and provides a comprehensive international survey of centres that compile, evaluate and publish numerical data for science and technology. Various sections of the book cover National Data Programmes in the U.K., U.S.A. and U.S.S.R.; centres covering very broad areas of science, for example, Landolt-Börnstein; specialised numerical data projects and their publications; a survey of handbooks providing data summaries in chemistry, physics, biology, earth sciences and analytical chemistry; and a brief guide to sources of internationally approved units, symbols, constants and nomenclature.

The most extensive section of the book deals with Numerical Data Projects on specialised topics. These include nuclear, atomic and molecular properties; infrared, microwave, Raman, ultraviolet, visible, mass and nuclear magnetic resonance spectra; the solid state including crystallographic, mineralogical, electrical and magnetic properties, superconductive materials, etc.; thermodynamic, transport and solution properties; chemical kinetics; gas chromatography; optical rotatory powers; colloid and surface properties; and a number of other specialised areas. For example, under Mass Spectra, separate entries deal with "Selected Mass Spectral Data" produced by the American Petroleum Institute, "Selected Mass Spectral Data" produced by the Thermodynamics Research Centre Project (formerly the Manufacturing Chemists Association), the

Compilation of Mass Spectral Data from Grenoble, and the Aldermaston/OSTI Mass Spectrometry Data Centre. The section on nuclear magnetic resonance spectra deals with the spectral data projects operated by the American Petroleum Institute, the Thermodynamics Research Centre and Sadtler Research Laboratories, and the high resolution n.m.r. spectra catalogues produced by Varian Associates and by Japan Electron Optics Laboratory Co. Ltd. Each entry is discussed under four headings: (i) "Organisation" gives a brief description of the organisation under which the work is carried out, including the director, number of staff, sources of finance, etc., as appropriate; (ii) "Coverage" defines the range of materials covered, their states and experimental conditions, where appropriate; (iii) "Analysis" gives a statement of the objectives of the data centre, together with some assessment of the quality of the data; and (iv) "Publications" gives information on sources of publications and their costs.

Over-all the book covers the organisation, scope and publications of some 150 data centres and projects in 26 countries, and also lists about 120 handbooks. The prime emphasis is on projects that systematically extract, evaluate and publish data in selected fields, on a regular basis; centres maintaining files of data, but answer questions only on request, and publications that are not readily available, are excluded. The subject areas are less extensive than those covered by the OSTI publication "Data Activities in Britain," but the very deep international coverage meets a long-standing requirement, and it is pleasing to note that revisions are already planned at 2-yearly intervals. The book includes no direct numerical data, but its comprehensive listing of sources should provide the starting point for an efficient search, and as such it will form a particularly useful reference volume for all scientists and engineers who require reliable data for calculations and research.

R. K. WEBSTER

PHOTOMETRIC METHODS OF ANALYSIS. By A. B. CALDER, B.Sc., Ph.D., F.I.S., F.R.I.C. Pp. iv + 312. London: Adam Hilger Ltd. 1969. Price 104s.

The stated aim of this book is to discuss emission and absorption photometric methods of analysis for workers both in research and industrial laboratories as well as for undergraduate and postgraduate students. This covers a very wide field indeed—a survey of a recent issue of *Chemical Abstracts* showed that two out of every five abstracts were concerned with photometry of one sort or another—and so it is inevitable that in a volume of this size the coverage must be either cursory or else highly selective.

The book begins with a brief account of spectral theory (12 pages). This is followed by a useful introduction to emission-spectrographic techniques in which arcs or sparks are used as excitation sources (75 pages). The sections on photographic photometric techniques and quantitative analysis are particularly good, but it is a pity that the coverage has not been extended to more recent methods of excitation, such as the use of pulsed lasers or plasma sources. Chapter 3 (27 pages) is on flame-emission spectroscopy and includes 6 pages on atomic-absorption spectroscopy, but is too short and insufficiently up to date to be of much practical use. Chapter 4 (60 pages) is concerned with absorption-photometric methods of analysis, and includes accounts of infrared as well as visible and ultraviolet spectroscopy. The quantitative aspects are dealt with authoritatively and in depth, but at the expense of the qualitative and structural aspects. Chapter 5 (12 pages) deals briefly with colorimetry and abridged spectrophotometry, including turbidimetry, nephelometry and fluorimetry. Chapter 6 is the longest and undoubtedly most useful chapter of the book (77 pages). Entitled "Evaluation and presentation of photometric analytical data," it begins with a statistical treatment of errors, then proceeds to apply the principles discussed to obtaining the maximum information from photometric data, and concludes with a discussion of mechanical aids for photometric calculations. The book concludes with some worked problems and practical exercises, spectrographic analytical data, statistical tables, and so on. There is also a supplementary reading list.

The coverage of this book is uneven. Thus, although the more classical techniques (*i.e.*, emission spectrography and molecular-absorption photometry) are discussed in fair detail, more recent techniques, such as fluorimetry and atomic-absorption spectroscopy, are not really discussed in any useful depth. The book concentrates on the techniques involved, such as sample pre-treatment and the design of quantitative procedures, and has a special emphasis on the mathematical evaluation of photometric data. This latter aspect is dealt with most authoritatively. On the other hand, there is little discussion of instrumentation, and a systematic cataloguing of standard methods of analysis of individual elements is not included.

It would have been better if this book had either been designed intentionally as a general introduction to all forms of photometric analysis, suitable for students and non-experts in the subject, or else if it had dealt with some particular aspect in depth, such as atomic-spectroscopic methods or the mathematical evaluation of photometric data and the design of photometric experiments. As it is, the appeal of the book seems to be divided between specialist and general reading.

The presentation is adequate, only a few errors in the text being noted, but the quality of the diagrams is disappointing, some of the legends accompanying them being quite inadequate. The index is far from comprehensive.

R. G. ANDERSON

MODERN METHODS IN ORGANIC MICROANALYSIS. By JEAN P. DIXON. Pp. xviii + 301. London, Princeton, New Jersey and Toronto: D. Van Nostrand Company Ltd. 1968. Price 70s.

This is a book that deals with organic microchemistry in a pragmatic manner, depending largely on the author's wide practical experience of the subject for what is included and what is omitted. It is primarily a book for the technician and for the undergraduate although, no doubt, even the more experienced graduate will find in it much of interest. It is, above all else, very readable and worth reading.

The first ten chapters cover the subjects, laboratory design and equipment, sampling (by which is meant weighing), carbon and hydrogen, nitrogen, oxygen, sulphur, halogens, phosphorus and boron, and they are well written and informative. The subsequent six chapters, covering the determination of metals in organic compounds, potentiometry in non-aqueous media, miscellaneous determinations, quantitative paper and thin-layer chromatography, instrumentation and automation and, lastly, accuracy and sources of error, are all too short to offer a really adequate treatment to any. On the dust-cover, the publishers inform the reader that this is a book with a comprehensive and critical coverage of the latest techniques in microanalysis. How can the determination of metals, from sodium to uranium, be comprehensively and critically covered in 7 pages, or even organic functional-group analysis in 34 pages? Disappointing, too, is the chapter concerning automation: how invaluable would a critical assessment of C.H.N. analysers have been, in addition to the catalogue of instruments and the principles on which they operate that is presented. Finally, one is tempted to ask why a whole chapter is devoted to quantitative paper and thin-layer chromatography while no comparable chapter is given to gas chromatography.

The index is surprisingly short and incomplete; it is about half the length of the list of contents, which is remarkably detailed. This has the disadvantage that particular topics are often difficult to locate unless one is very familiar with the text. On the other hand, many techniques, for example, combustion in the oxygen-filled flask, are spread over several chapters and the cross-referencing is generally well done.

J. S. WRAGG

INSTRUMENTAL METHODS IN CHEMICAL ANALYSIS. THIRD EDITION. By GALEN W. EWING. Pp. x + 627. New York, St. Louis, San Francisco, Toronto, London and Sydney: McGraw-Hill Publishing Co. Ltd. 1969. Price 137s.

This book sets out to survey modern analytical instruments and analytical techniques and is intended for use as a text-book by undergraduate and graduate students. For this purpose it is eminently suitable. The author provides sufficient theory for the understanding of the principle of each instrument or method, gives excellent descriptions of instruments typical of their class and, most important, provides sufficient interpretative data and information about applications to enable the reader to assess the true value of a particular method in comparison with the available alternatives.

After an introductory chapter, the following nine chapters are devoted to optical methods, including ultraviolet and visible absorption, fluorimetry and phosphorimetry, infrared absorption, light scattering, emission and flame spectroscopy, X-ray methods, polarimetry and optical rotatory dispersion. The series of five chapters which follows deals with electrochemical methods of analysis, including potentiometry, voltammetry, polarography, electro-deposition, coulometry and conductimetric methods. Separate chapters are devoted to the discussion of radioactivity as an analytical tool, magnetic resonance spectroscopy and thermometric methods. A section dealing with the separation techniques, gas chromatography, liquid chromatography, solvent extraction and related methods, and electrical separation procedures, then follows, and finally two very useful chapters dealing with general considerations in analysis and the electronic circuitry of analytical instruments are presented.

Each chapter concludes with some problem questions designed to further the understanding of the subject matter covered in the text. The book includes a practical section, the experiments in which are intended to emphasise the principles involved and the analytical importance of sample preparation, the adjustment of measurement conditions and the methods of treatment of the measured results.

In this third edition of a book covering the ever expanding field of instrumental methods of chemical analysis it is understandable that the author has chosen to make a reduction in the space given to such techniques as potentiometric and conductimetric titrimetry, refractometry and emission spectrography. This has allowed a fuller treatment of gas chromatography, recent advances in polarography and related methods, and the introduction of such new subjects as optical rotatory dispersion, circular dichroism, microwave absorption and chronopotentiometry.

This volume is as up to date as any text-book of such a high quality could be; it contains a good bibliography and is adequately indexed. The text is clearly printed and well illustrated and is written in a readable style that will capture and hold the interest of the student.

D. C. M. SQUIRRELL

ORGANIC ELECTRONIC SPECTRAL DATA. Volume 5. 1960-1961. Edited by J. P. PHILLIPS, ROBERT E. LYLE and P. R. JONES. Pp. vi + 1019. New York, London, Sydney and Toronto: Interscience Publishers, a division of John Wiley & Sons. 1969. Price £16 8s.

This is the fifth volume in a valuable series. The data now come from over seventy journals. Several of those formerly searched have been omitted and a few new ones included. The series of five volumes provides information on over 100,000 compounds. Three more volumes are in preparation. The editors estimate that the effort to cover all of the literature containing spectra may not be more than 95 per cent. successful. The proportion of compounds that escapes the net must, however, be quite small as spectra of new substances frequently appear in more than one publication.

The series, including Volume 5, is proving reliable and convenient to use.

R A. MORTON

ANALYSIS OF ORGANOALUMINIUM AND ORGANOZINC COMPOUNDS. By T. R. CROMPTON, B.Sc., F.R.I.C. Pp. xiv + 354. Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris and Braunschweig: Pergamon Press. 1968. Price 126s.; \$16.

The analysis of organoaluminium compounds is not something one undertakes lightly as, apart from being extremely hazardous in the hands of the uninitiated, they are compounds that, for a successful analysis, demand the strictest attention to detail. Mr. Crompton has had considerable experience in this field, he is fully aware of all the difficulties and, in view of the increasing use being made of these compounds, he has earned our gratitude for writing this book. In each chapter, specific determinations are discussed followed, where relevant, by detailed methods written in the standard I.S.O. form (or slight variations thereof). Great stress is laid on safe operation. Thus, careful study of the text with one or two trial runs should give the reader sufficient confidence to tackle any particular analysis and get meaningful results. The sampling described in these methods refers to the taking of the particular portion for analysis which is, of course, very important. It would have been instructive to have details of how samples are taken from, say, ton quantities as someone must have to do this!

The larger part of the book is concerned with aluminium compounds. The first two chapters deal with the determination of alkyl and alkoxide groups up to $C_{20} - C_{30}$ and hydride groups, while the third chapter describes the determination of aluminium, halogens and aluminium-bound amino and thioalkoxide groups. The next five chapters deal with the use of a number of analytical techniques in the study of aluminium compounds, including conductimetric, potentiometric, complexometric, dielectric constant and thermometric titration, infrared, ultraviolet and visible spectrophotometry, Raman, nuclear magnetic resonance and magnetic proton resonance spectroscopy. The analysis of organozinc compounds, which has not received as much attention as that of aluminium compounds, is described in the final chapter.

The literature of this corner of analytical chemistry is not large and it is growing only slowly so that this excellent book is likely to be the standard work on the subject for some time to come.

A. G. JONES

AN INTRODUCTION TO THERMOGRAVIMETRY. By C. J. KEATTCH, F.R.I.C. Pp. vi + 59. London: Heyden & Son Ltd. 1969. Price \$4.50.

This book is the fifth in a series of introductory texts. In the foreword we read, "Yet thermogravimetry is a powerful technique in its own right," and Mr. Keattch is to be congratulated for providing this introductory booklet, which in small compass not only covers basic aspects of choice of apparatus, but also gives insight into the wide range of problems (from polymer science to reaction kinetics) in connection with which thermogravimetric information may be of value."

This provides a good summary of this useful book. Within its 59 pages there is a brief introduction to the following topics: origins, thermobalances, thermogravimetric data, interpretation of data, applications to inorganic chemistry, to organic and polymer chemistry, and to minerals and applied sciences, while an appendix lists the currently available commercial thermobalances.

In general, the author strikes a nice balance in his treatment of the wide range of applications, except that the organic range of applications is very briefly treated. The necessity to keep the accounts short has resulted in one or two generalisations which ought to be challenged, for example, on p. 17, "The shape of the thermogravimetric curve is a function of the reaction kinetics," is only partly true and the important influence of environmental factors has not been stressed sufficiently. However, a too facile treatment has been avoided and the book is well documented and gives an adequate lead-in to the literature of the subject. Perhaps the best judge of such a book is someone who is coming new to the subject, and one such person commented that he had found the book "most helpful."

The fact that the publishers could not adopt the recommendations of the Nomenclature Committee of the International Confederation of Thermal Analysis is a serious blemish on what is otherwise an excellent introduction to the subject, clearly presented and with few typographical errors. It is to be recommended to all those who are investigating the possibility of using this particular thermoanalytical technique.

J. P. REDFERN

LABORATORY PROCEDURES: WEIGHING. By J. DAVIES and J. W. OWEN. Pp. viii + 48. London: Sir Isaac Pitman & Sons Ltd. 1969. Price 16s.

LABORATORY PROCEDURES: PIPETTE, VOLUMETRIC FLASK AND BURETTE. By J. DAVIES and J. W. OWEN. Pp. ix + 93. London: Sir Isaac Pitman & Sons Ltd. 1969. Price 25s.

The declared aim of these two books from the Pitman Series of Programmed Texts is to teach basic laboratory techniques. The texts have been tested on students following the City and Guilds No. 119 Course in the Science Laboratory Technicians Ordinary Certificate at Paddington College of Further Education, with commendable results.

Attractively produced, with plenty of photographs and diagrams, the instructions seem clear and unambiguous. Attitudes to programmed learning will vary, but even in traditional teaching laboratories it would be useful to have several copies of these manuals available for students having difficulties.

B. J. MOODY

Errata

JULY (1967) ISSUE, p. 471, under "CALCULATION." For

$$\frac{0.008 (A_x - A_b) \times W}{(A_s - A_b)} \quad \text{read} \quad \frac{0.008 (A_x - A_b)}{(A_s - A_b) \times W}$$

APRIL (1970) ISSUE, p. 360, Table II. Under "Seed dressing No. 1," "Seed dressing No. 3," "Wheat bulb fly dressing No. 1" and "Wheat bulb fly dressing No. 2," for "mineral filters" read "mineral fillers."

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Supplement to Official, Standardised and Recommended Methods of Analysis

Compiled and Edited by

S. C. JOLLY, B.Pharm., B.Sc., F.R.I.C., M.P.S.

Pp. xiv + 424

In 1963 the Analytical Methods Committee of the Society for Analytical Chemistry published a collection of all its standardised methods of analysis and a comprehensive bibliography of official and recommended methods of analysis under the title "Official, Standardised and Recommended Methods of Analysis." Now, 4 years later, a Supplement to this volume has been produced that contains the more recently standardised methods of analysis published by the Committee, a re-written and re-set version of the bibliography and an index to the main volume and to the Supplement.

All 44 sections of the bibliography in the 1963 volume, except that on Soils, have been revised, and a new section on Coffee has been added. The information in most of these sections is now correct up to the end of 1966 and in some instances later; for no section is the date earlier than June 1966. The comprehensive index provided covers those parts of the main volume that are still applicable and the whole of the Supplement.

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Evaluation and Correction of Interference between Aluminium, Silicon and Iron in Atomic-absorption Spectrophotometry

Inter-element interference in the determination of aluminium, silicon and iron in pyrophosphate solutions has been investigated. The maximum concentrations were 100 p.p.m. of aluminium, 117 p.p.m. of silicon and 50 p.p.m. of iron; the tetrasodium pyrophosphate was 7.5×10^{-3} M. In the determination of aluminium, silicate depressed the absorption, while iron did not interfere. Both aluminium and iron enhanced the absorption in the determination of silicon, and in the determination of iron, both aluminium and silicon depressed the absorption. Absorbance data, representing analytical results on some 215 solutions, were fitted to equations containing so-called interference coefficients. With this approach, corrections for inter-element interference are easily made.

A. P. FERRIS, W. B. JEPSON and R. C. SHAPLAND

Central Laboratories, English Clays Lovering Pochin & Co. Ltd., St. Austell, Cornwall.

Analyst, 1970, **95**, 574-578.

Non-aqueous Atomic-absorption Spectrophotometric Determination of Organometallic Biocides

Absorbance results obtained by non-aqueous atomic-absorption spectrophotometry for organotin and organolead biocides have provided calibration graphs that permit quantitative determination of these substances. In a particular application a method is given for measuring the amount of tributyltin chloride recoverable from that deposited on wool under prescribed conditions.

G. N. FREELAND and R. M. HOSKINSON

Division of Textile Industry, C.S.I.R.O., Geelong, Victoria, Australia.

Analyst, 1970, **95**, 579-582.

Evaluation of 2-Hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic Acid and Hydroxynaphthol Blue as Metallochromic Indicators in the EDTA Titration of Calcium

The acid dissociation constants and the chelate stability constants for calcium have been determined spectrophotometrically on purified samples of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Patton and Reeder's dye) (HSN) and hydroxynaphthol blue, both of which have been used as indicators in EDTA titrations of calcium. By comparison of experimental and theoretical curves of the indicator colour change at the end-point, it was found that these two dyes are suitable indicators for the titration of calcium at pH 12 to 13, with a slightly more satisfactory end-point indication given by hydroxynaphthol blue.

ATUKO ITOH and KEIHEI UENO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.

Analyst, 1970, **95**, 583-589.

4-Nitrophenylacetonitrile, a Sensitive Reagent for Quinones, Hydroquinone and Pyrocatechol

A new test for quinones, hydroquinone and pyrocatechol is based on the reaction with 4-nitrophenylacetonitrile and alkali.

L. LÉGRÁDI

Nitrokémia Industrial Plants, Fűzfőgyártelep, Hungary.

Analyst, 1970, **95**, 590-591.

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Determination of Water-soluble Sulphate in Acidic Sulphate Soils by Atomic-absorption Spectroscopy

A method is described for the determination of water-soluble sulphate in soil extracts. After a preliminary conductivity measurement to determine the size of the aliquot to be taken, the sulphate is precipitated by the addition of a known amount of barium chloride. The excess of barium remaining in solution is determined by atomic-absorption spectroscopy and the sulphate content deduced. The method is rapid and compares well with the conventional gravimetric method.

J. A. VARLEY and POON YEW CHIN

Harrison and Crosfield (Malaysia) Sdn. Bhd., Oil Palm Research Station, Banting, Selangor.

Analyst, 1970, **95**, 592-595.

Adaptation of the Bergman and Loxley Technique for Hydroxyproline Determination to the AutoAnalyzer and its Use in Determining Plasma Hydroxyproline in the Domestic Fowl

The adaptation of a manual technique for hydroxyproline determination to the AutoAnalyzer is described. The method can be used to determine standard solutions to within 2.6 per cent. and to deal with successive concentration differences of up to 10 $\mu\text{g ml}^{-1}$. The concentration range for optimum accuracy is 2.5 to 15.0 $\mu\text{g ml}^{-1}$. Application of the technique to the study of plasma hydroxyproline levels in the domestic fowl is described, and comparison with isotope-dilution analysis demonstrates the lack of gross interference.

D. W. BANNISTER and ANNE B. BURNS

Agricultural Research Council, Poultry Research Centre, King's Buildings, West Mains Road, Edinburgh 9.

Analyst, 1970, **95**, 596-600.

Determination of Total Nitrogen, Phosphorus and Iron in Fresh Water by Photo-oxidation with Ultraviolet Radiation

The photo-oxidation method described by Armstrong, Williams and Strickland for determining total phosphorus and nitrogen in sea water has been adapted for analysis of fresh-water samples and extended to include the determination of total iron. The samples are subjected to ultraviolet irradiation in a photochemical reactor consisting of a high pressure mercury-arc lamp, a reactor body with twenty-four fused silica sample tubes and a cooling fan. Organically combined phosphorus and iron are converted into orthophosphate and iron(III) ions in the presence of acid and excess of oxygen after an irradiation time of 1 hour. Organonitrogen compounds and ammonia in solutions with pH range 6.5 to 9 are oxidised to nitrate and nitrite after 4 hours' irradiation in the presence of excess of oxygen, which excess is ensured by addition of a few drops of 30 per cent. hydrogen peroxide solution.

A. HENRIKSEN

Norwegian Institute for Water Research, Oslo 3, Norway.

Analyst, 1970, **95**, 601-608.

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The Use of Paired Ion-sensitive Electrodes to Measure Gradients of pH and of Sodium and Chloride Ions across Actively Transporting Membranes

A method is described in which pairs of ion-sensitive electrodes are used to determine changes in the concentration gradients of pH and of Na⁺ and Cl⁻ ions across an actively transporting membrane. Measurements can be made almost continuously without withdrawing samples. Matched pairs of ion-sensitive electrodes are placed in the membrane chambers with one of each pair on each side of the membrane. A procedure is described by which the potential difference can be measured across these pairs of high-impedance electrodes. The potential difference generated across the transporting membrane is measured independently. From these two sets of values the concentration gradients of H⁺, Na⁺ and Cl⁻ ions across the membrane can be calculated. This method registers gradients of 0.02 pH unit and of 0.5 milli-equivalents l⁻¹ of Na⁺ and Cl⁻; the changes in ionic concentration can be correlated with the membrane potential almost continuously. Short-circuit current cannot be measured with the electrodes *in situ*. Absolute ionic concentrations in the solutions can be measured at any time by using a standard reference electrode with any of the other electrodes.

D. M. NUTBOURNE

Medical Research Council, Department of Experimental Medicine, University of Cambridge.

Analyst, 1970, **95**, 609-613.

A Simple Colorimetric Method for the Determination of Iron in Serum

Iron in serum is freed from its attachment to protein with hydrochloric acid and the proteins are precipitated with trichloroacetic acid. A coloured complex is formed with metamizol in the presence of a high concentration of hydrogen peroxide, the absorption maximum at 440 nm being used for its colorimetric determination. The complex is relatively stable and its absorption obeys Beer - Lambert's law up to 400 µg of iron per 100 ml. Recovery experiments and comparison of a series of determinations with a widely used colorimetric method showed no statistical difference from expected values.

FAYEZ K. GUIRGIS and YEHIA A. HABIB

Departments of Clinical Pathology and Physiology, Faculty of Medicine, Alexandria, U.A.R.

Analyst, 1970, **95**, 614-618.

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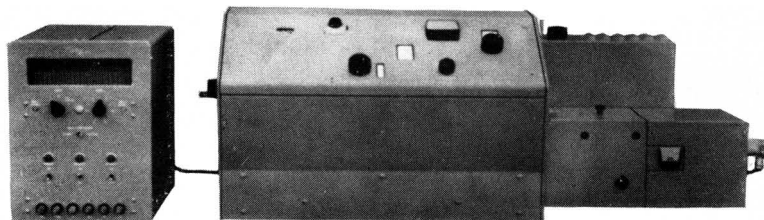
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