ANALYTICA CHIMICA ACTA

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Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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Completing Volume 37

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1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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INORGANIC ION EXCHANGERS

Topics in Inorganic and General Chemistry, Monograph 2

by C. B. AMPHLETT, Ph.D., D.Sc.
Chemistry Division, Atomic Energy Research Establishment, Harwell, Berks., Great Britain

5½ x 8½, xi + 141 pages, 32 tables, 36 illus., 193 lit.refs., 1964, Dfl.22.50, 50s., US$8.00

Interest in inorganic ion-exchangers (natural and synthetic) was recently renewed when certain drawbacks of organic ones became apparent. The author has dealt with inorganic exchangers as a class, and includes fundamental studies on problems of inorganic and structural chemistry, mineralogy and geochemistry, as well as practical applications.

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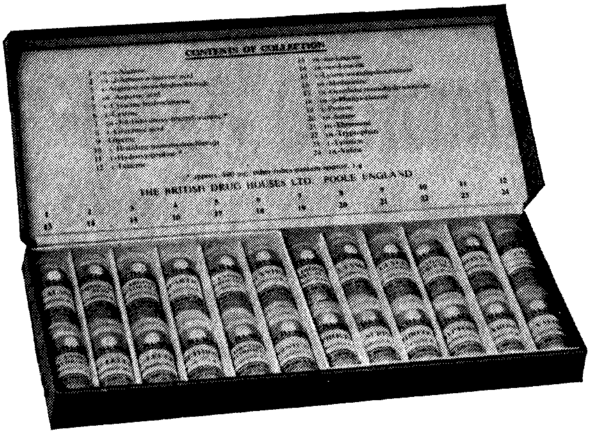

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In recent years Japan has been seen to emerge as the scene of most significant contributions to modern research in muscle biochemistry. Since the discovery of the particulate relaxing factor in 1955, the horizon of interest has widened to include a variety of topics in muscle biochemistry ranging from the theoretical to the biochemical. It can now be safely said that the status of Japan in this area of modern advance is firmly established. Over the years, contacts and friendships have steadily developed between the Japanese and their colleagues in other countries and the present book is an excellent manifestation of this cooperation. Representatives of many leading centres throughout the world have ensured the presentation of a full and stimulating review of the progress at the major frontiers of muscle research which the last few years have seen.

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Volume 10

edited by
V. V. KONINGSBERGER and
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To meet an urgent need felt by those working in the field of nucleic acids and protein synthesis, a symposium was held in Lunteren, The Netherlands, in June, 1966, to consider specific aspects of regulatory mechanisms in this area of biochemistry. Investigations have developed very rapidly in recent years and were thought to have reached the stage where these intricate processes could profitably be discussed among the leading investigators. The papers presented at this symposium form the basis of this book. A total of 34 papers are presented reporting genetic, enzymological and pure biochemical studies on a variety of bacterial, viral and animal-cell systems. The contributors represent the major research institutes which have set themselves the task of elucidating the basic problems in this field. Thus, in spite of the limits set by the general title, a very wide range of interest is covered, enabling the reader to take a broad view of a vast subject at an exciting stage in its development.

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X-RAY EMISSION SPECTROGRAPHY IN GEOLOGY

Methods in Geochemistry and Geophysics, 4

by I. ADLER
National Aeronautics and Space Administration,
Theoretical Division, Goddard Space Flight Center,
Greenbelt, Md., U.S.A.

5½ x 8½″, xii + 258 pages, 33 tables, 86 illus., 1966, 90s., US$16.50, Dfl.45.00

X-ray emission analysis (fluorescence and electron probe) has become an extremely powerful analytical technique for the geochemist. It is important that its principles should be clearly stated if full advantage is to be taken of the technique.
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 37, No. 4, April 1967

THE MECHANISMS OF INTERFERENCE EFFECTS AND THEIR ELIMINATION IN THE DETERMINATION OF ALKALINE EARTH METALS BY FLAME PHOTOMETRY

The depressing effect of aluminum on the signal of alkali earth metals in an acetylene–air flame with a spray chamber and the various possibilities of eliminating this interference were investigated. The importance of processes taking part in the crystalline aerosol particles before volatilization, as revealed by flame profiles is emphasized, and appropriate mechanisms for the depressing effect and its elimination are suggested.

I. Rubeška and B. Moldan,
Anal. Chim. Acta, 37 (1967) 421–428

USE OF A CONTINUOUS SOURCE OF EXCITATION, AN ARGON–HYDROGEN–AIR FLAME, AND AN EXTENDED FLAME CELL FOR ATOMIC ABSORPTION FLAME SPECTROPHOTOMETRY

A continuous source of excitation in conjunction with an argon–hydrogen–entrained air flame, an extended flame cell, a medium-dispersion monochromator and a typical detection system is shown to give good sensitivities for the atomic absorption flame spectrophotometric measurement of 21 elements. Useful working curves over a 100-fold concentration range are obtained for each of the 21 elements using the simple experimental system. The advantages gained with this system are discussed

W. W. McGee and J. D. Winefordner,
Anal. Chim. Acta, 37 (1967) 429–435

COMPARISON OF LINE AND CONTINUOUS SOURCES IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

Expressions are given for the absorption signal (absorbance or fraction absorbed) in atomic absorption spectrophotometry with a line source and a continuous source, respectively. A theoretical and experimental comparison is made between the shape of the working curves, the magnitude of the signals, and the limits of detection in both cases. The significance of the spectral bandwidth of the monochromator and the absorption line profile is discussed. With a good medium-dispersion monochromator, a continuous source offers several distinct advantages and yields detection limits which are approximately the same as those obtained with a hollow-cathode discharge tube.

L. de Galan, W. W. McGee and J. D. Winefordner,
Anal. Chim. Acta, 37 (1967) 436–444

HIGH-PRECISION ANALYSIS OF NUCLEAR MATERIALS BY CONSTANT-CURRENT COULOMETRY

PART I. DETERMINATION OF URANIUM

Work is described on the application of constant-current coulometry for the highly precise and accurate assay of uranium and its compounds. Uranium is reduced to the tetravalent state by titanium(III) in nitric acid solution containing sulphamate and reacted with excess of iron(III) to give an equivalent amount of iron(II) which is titrated with electrogenerated cerium(IV). Factors governing the overall titration efficiency are discussed and results for the assay of a number of standard uranium materials presented. The procedure gives a standard deviation of 0.004% at the 50-mg level and an accuracy exceeding 0.01%.

G. C. GOODE, J. HERRINGTON AND W. T. JONES,
Anal. Chim. Acta, 37 (1967) 445–454

COULOMETRIC DETERMINATION OF ALKALOIDS AND ORGANIC BASES AFTER PRECIPITATION AS TETRAPHENYLBORATES

(in French)

A coulometric microdetermination of salts of certain organic bases and alkaloids is described, based on precipitation as the tetraphenylborates and the coulometric determination of the tetraphenylborate content of the precipitate with electrogenerated silver ion. Eleven compounds were determined with satisfactory accuracy.

G. J. PATRIARCHE ET J. J. LINGANE,
Anal. Chim. Acta, 37 (1967) 455–459

FLUORIMETRIC DETERMINATION OF LITHIUM WITH DIBENZOTHIAZOLYLMETHANE

Lithium is determined by measuring the fluorescence produced on reaction with dibenzothiazolylmethane; zinc is the only other metal that fluoresces. The practical limits for the determination of lithium in salts are from 0.5 to 20 μg although 0.01 μg can be determined in pure solutions.

A. E. PITTS AND D. E. RYAN,
Anal. Chim. Acta, 37 (1967) 460–464

THE APPLICATION OF RESONANCE MONOCHROMATORS TO THE DETERMINATION OF LITHIUM IN BLOOD SERUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Lithium in blood serum can be determined rapidly and with sufficient accuracy by atomic absorption measurement of solutions of blood serum diluted with water, using either a conventional atomic absorption spectrophotometer or one with a resonance monochromator. Calibrating solutions contain sodium and potassium at approximately the concentrations present in the serum solutions as these metals cause a slight enhancement of lithium absorption in the air/coal gas flame. Results are reproducible to within ±0.2 μg Li/ml in the serum and the limits of sensitivity attainable for samples diluted 1:10 are 0.3 μg Li/ml in the serum with the conventional instrument and 0.6 μg Li/ml in the serum with the resonance monochromator.

J. A. BOWMAN,
Anal. Chim. Acta, 37 (1967) 465–471

SEPARATION OF SOME ORGANIC MIXTURES BY FRACTIONAL ENTRAINMENT SUBLIMATION

Fractional entrainment sublimation has been successfully applied to mixtures of sublimable organic compounds. The components of the mixtures were obtained in well-defined crystalline zones, sufficiently pure for identification by melting points and spectroscopic analysis. The highest temperature limit of any zone was reproducible and may be comparable to the well known R_F value for qualitative analytical purposes. The technique was employed for the separation of 11 artificial mixtures and the purification of 5 crude reaction products. Samples of 10–60 mg were easily separated. The apparatus, operating procedures, and some of the factors which influence the separations are discussed.

K. P. REED AND E. W. BERG,
Anal. Chim. Acta, 37 (1967) 472–479

ABSORPTIOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM WITH RHODAMINE B

Uranium(VI) can be extracted as a complex with rhodamine B into a benzene–ether–hexone solvent from a benzoate buffered solution. Optimum conditions for the colour development are defined, leading to a molar absorptivity of 102700 $\text{mmol}^{-1}\,\text{cm}^2$ at 555 nm, the highest yet reported for a uranium complex. The determination of uranium in the range 0.02–3 μg/ml in nitrate samples is described. The relative standard deviation ranges from 20 to 0.6%. The interference of several ions is investigated.

H. H. PH. MOEKEN AND W. A. H. VAN NESTE,
Anal. Chim. Acta, 37 (1967) 480–483

DETERMINATION OF HYDROXYLAMINE WITH NESSLER REAGENT

Hydroxylamine forms strong color complexes with ninhydrin and Nessler solution, two of the standard reagents for ammonia. In the case of ninhydrin, ammonium salts and hydroxylamine have the same molar absorptivity; hydroxylamine is probably reduced to ammonia and measured as such. With Nessler reagent, hydroxylamine has 5 times the molar absorptivity of ammonia at low concentrations; levels above 10 μM result in reagent precipitation, because of a redox reaction involving oxidation of hydroxylamine to nitrite and reduction of Nessler reagent. The conditions of Nesslerization can be altered to provide a specific assay for hydroxylamine in the range of 5–50 μM, with no absorbance being produced by ammonium salts. Other hydroxylamine derivatives give no color reactions with ninhydrin or Nessler reagent.

W. N. FISHBEIN,
Anal. Chim. Acta, 37 (1967) 484–489

THE DETECTION OF OXYGEN IN ORGANIC COMPOUNDS WITH POTASSIUM TETRATHIOCYANATO-COBALTATE(II)

A new micro or semimicro test for detection of oxygen in organic compounds is based on the blue colour given on treatment with a solid potassium thiocyanato-cobaltate reagent. The test was checked with *ca.* 500 compounds containing various functional groups; very few anomalous reactions were observed.

F. BUSCARÓNS AND M. PAREIRA,
Anal. Chim. Acta, 37 (1967) 490–496

COMPLEXES OF ORGANOLEAD AND ORGANOTIN IONS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

The stability constants of the complexes of 1-(2-pyridylazo)-2-naphthol with several organotin and lead ions were determined spectrophotometrically in aqueous 20% (v/v) dioxane and were shown to have very high values. The extraction of the complex of $(C_2H_5)_2Pb^{2+}$ from water into chloroform was studied, and the formation of an extractable $(C_2H_5)_2Pb(PAN)(OH)$ complex is postulated.

G. PILLONI,
Anal. Chim. Acta, 37 (1967) 497–507

SIMULTANEOUS DETERMINATION OF FLUORINE AND CHLORINE IN SILICATE ROCKS BY A RAPID SPECTROPHOTOMETRIC METHOD

A rapid accurate method is described for simultaneous determination of fluorine and chlorine in silicate rocks by taking separate aliquots of the single sample dissolution. Fluorine, without separation, was determined by means of the zirconium–eriochrome cyanine R complex, whereas chlorine was determined by means of the stable iron(III) thiocyanate complex. The method was tested with standard rocks. Results with geochemical standards were comparable with analyses reported by others. Application to several acidic, mafic, and ultramafic rock samples gave results with a relative standard deviation of less than 5%.

W. H. HUANG AND W. D. JOHNS,
Anal. Chim. Acta, 37 (1967) 508–515

QUINOLINIUM AND LUTIDINIUM MOLYBDATES AS REAGENTS FOR THE PRECIPITATION OF PHOSPHATE

The precipitation of phosphate with quinolinium molybdate was studied by means of radioactive tracers, in relation to the excess of reagent, temperature of precipitation, etc. Precipitation is almost quantitative (99.3%) even with a stoichiometric amount of reagent added but an excess helps to minimise the inhibitory effects of certain ions, notably Fe^{3+}; inhibitory effects are eliminated by digesting the solution for 2 h. Chromium(III) nitrate, nickel(II) nitrate and manganese(II) nitrate have relatively little effect on the precipitation of quinolinium molybdophosphate. Under the conditions required for the quantitative precipitation of phosphorus, arsenic is also quantitatively precipitated.

Phosphate can be precipitated as lutidinium molybdophosphate using 2,4-, 2,5- or 2,6-lutidinium molybdate; the reagents are less efficient than quinolinium molybdate but can be used to precipitate phosphate under conditions which leave arsenate in solution.

R. B. HESLOP AND E. F. PEARSON,
Anal. Chim. Acta, 37 (1967) 516–524

THE DETERMINATION OF PHOSPHORUS WITH ORGANIC BASE MOLYBDATES

A selection of organic nitrogen bases was examined for the precipitation of phosphomolybdate. α-Picoline (2-methylpyridine) proved superior to the well-established quinoline; it is slightly more sensitive for phosphate, much less sensitive to arsenate and silicate, and less affected by citric acid so that phosphate can readily be determined in presence of these ions. The reagent solution is stable for at least a month. The α-picoline phosphomolybdate could not be used gravimetrically but the conventional titrimetric finish was satisfactory. The method was applied to the microanalysis of organic compounds.

A. M. G. MACDONALD AND A.-M. RIVERO,
Anal. Chim. Acta, 37 (1967) 525–531

A RAPID EMPIRICAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF AMMONIUM, FLUORINE AND ZIRCONIUM IN AMMONIUM HEXAFLUOROZIRCONATE SOLUTIONS

(Short Communication)

H. H. PH. MOEKEN AND W. A. H. VAN NESTE,
Anal. Chim. Acta, 37 (1967) 532–534

2-NAPHTHYL-α-METHOXYACETIC ACID AS A REAGENT FOR SODIUM

(Short Communication; in German)

H. HOLZAPFEL, P. NENNING AND P. KRAMER,
Anal. Chim. Acta, 37 (1967) 535–538

CHEMICAL SEPARATION AND DETERMINATION OF SMALL QUANTITIES OF STRONTIUM AND CALCIUM

(Short Communication)

K. R. KAR AND G. SINGH,
Anal. Chim. Acta, 37 (1967) 538–540

THE DETERMINATION OF ZINC BY SUBSTOICHIOMETRIC ISOTOPE DILUTION. A NOTE

(Short Communication)

J. STARÝ AND J. RŮŽIČKA,
Anal. Chim. Acta, 37 (1967) 541

NOTE ON THE LACTONISATION OF HYDROXYETHYLENEDIAMINETRIACETIC ACID (HEDTA). THERMOGRAVIMETRIC AND SPECTROSCOPIC STUDIES

(Short Communication; in French)

E. MERCINY,
Anal. Chim. Acta, 37 (1967) 542–545

THE DETERMINATION OF BORON IN DILUTE AQUEOUS SOLUTIONS BY NEUTRON ACTIVATION ANALYSIS

(Short Communication)

W. A. CASSATT, JR., H. P. ESTEY AND R. SLOTT,
Anal. Chim. Acta, 37 (1967) 545–548

SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. Belcher
Professor of Analytical Chemistry,
The University of Birmingham, Great Britain

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THE MECHANISMS OF INTERFERENCE EFFECTS AND THEIR ELIMINATION IN THE DETERMINATION OF ALKALINE EARTH METALS BY FLAME PHOTOMETRY

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(Received August 30th, 1966)

The determination of alkaline earth elements by emission as well as absorption flame photometry is susceptible to many interelement effects. The depressive effect of sulphates, phosphates, aluminum, iron and other less common elements is well known[1,2]; several different approaches to the elimination of these interferences have been recommended[3-7], but there is little unanimity on the mechanism of these effects. Further investigation on these problems therefore seemed desirable.

The present studies were confined to aluminum as the interfering element and magnesium, calcium and strontium as analysed elements. Aluminum is by far the most important interfering element in the analysis of silicate rocks. However, the conclusions drawn from this investigation should have a more general validity.

EXPERIMENTAL

Apparatus

Most experiments were carried out with the Unicam SP 900 flame spectrophotometer. For some measurements the atomizer, spray chamber and burner from the Zeiss model III flame photometer were used instead of the original one. Magnesium was determined by atomic absorption using a home-made apparatus, based on a Zeiss monochromator SPM-1 or by adding a magnesium hollow-cathode lamp to the Unicam SP 900. In all cases a "normal" acetylene–air flame was used. The atomic lines Mg 2852 Å, Ca 4227 Å and Sr 4607 Å were measured.

All reagents were either Specpure (Johnson Matthey $CaCO_3$, $SrCO_3$) or analytical grade. Oxine was added as a 10% solution in azeotropic hydrochloric acid.

RESULTS AND DISCUSSION

It has been emphasized by several authors[3,8] that the evaporation rate of aerosol particles in the flame has a decisive influence on the signal of the alkaline earth elements, many times greater than on the signal of other elements. This is because the dissociation of alkaline earth oxides formed in the flame falls off steeply from the reaction zone upwards because of the falling temperature and growing oxygen content in the burnt gases. The maximum signal reached therefore depends strongly on the kinetics of evaporation. The evaporation rate depends naturally on the mean size of the particles reaching the flame and on the vapour tension of the particular compounds. The particle size spectrum of the aerosol does not change much under definite working conditions, but the vapour pressure may change a lot depending on the compounds formed after heating the crystallized salts. Direct measurements of these reactions are hard to carry out but some idea may be obtained from flame profiles.

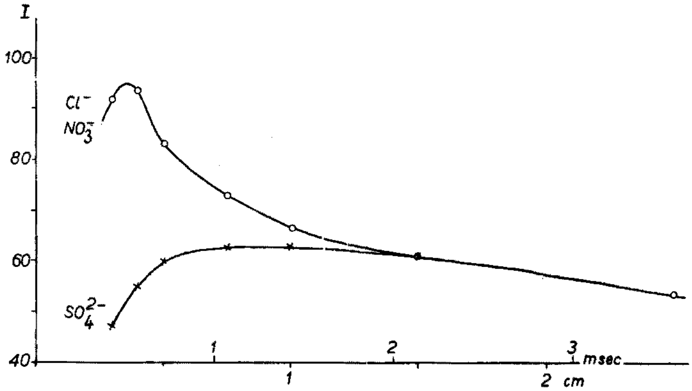

Fig. 1. The flame profile of magnesium with different anions. Emission of Mg 2852 Å measured from a flame column about 1 cm high; SP 900.

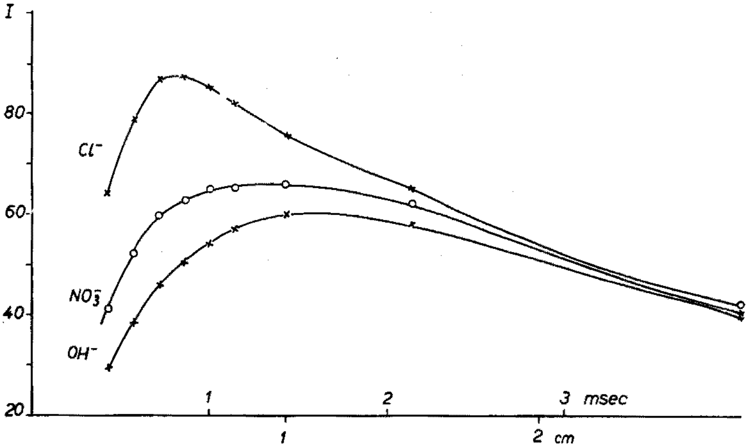

Fig. 2. Flame profile of calcium with different anions. Emission of Ca 4227 Å measured from a 1-cm high flame column; SP 900.

When the flame profiles* of different compounds of the alkaline earth elements are compared, some basic differences are at once evident. Whereas the flame profiles for magnesium chloride and nitrate are identical (Fig. 1), the flame profiles of the chloride and nitrate salts of calcium differ (Fig. 2). A similar difference was found for strontium chloride and nitrate. This may be easily explained as follows: calcium and

---

* Flame profiles may be measured either by emission or absorption. The absorption flame profile has a sharper maximum. The emission flame profile is slightly deformed by the temperature distribution in the flame which simultaneously causes a shift farther away from the burner head. In Figs. 1, 2 and 3, emission flame profiles are given.

strontium chlorides after crystallization as hydrates, release water molecules on heating and become the dehydrated chlorides, which volatilise much more easily than the respective oxides formed by the decomposition of nitrates. Magnesium chloride on the other hand releases hydrogen chloride on heating and changes to magnesium oxide in the same as magnesium nitrate[9]. Although calcium and strontium chlorides, on heating especially in presence of water vapour, also form the oxides, this reaction is evidently slower than the evaporation rate of chlorides. This simple mechanism explains the differences in emission of different calcium compounds.

Let us now consider the situation in presence of aluminum chloride and/or nitrate respectively. Aluminum salts, like magnesium salts, form aluminum oxide irrespectively of the anion present. Alumina reacts with the alkaline earth oxides forming very involatile aluminates[10] and as a consequence, the signals of the alkaline earth elements decrease with increasing aluminum concentration. The flame profiles for calcium and aluminum chlorides and calcium and aluminum nitrates (Fig. 3) show that the formation of involatile compounds is easier for the nitrates than for the chlorides. This indicates that the reaction involves only oxides and that the alkaline earth chlorides must undergo hydrolysis first. It is well known from inorganic chemistry, that this hydrolysis is catalysed by aluminum oxide so that the presence of aluminum salts probably speeds up this reaction.

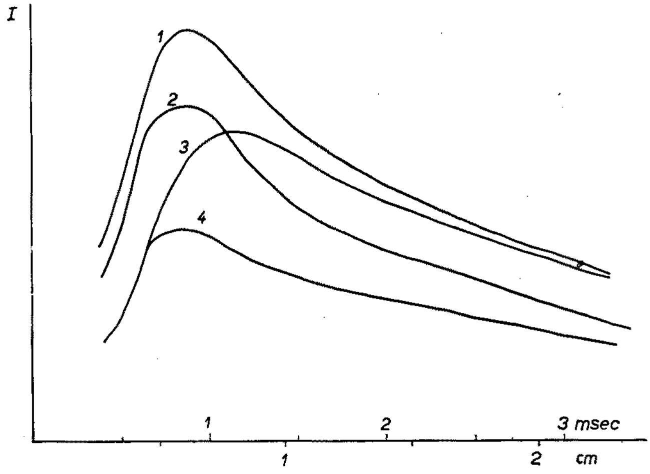

Fig. 3. Comparison of flame profiles of calcium chloride and nitrate in absence and presence of aluminum chloride and nitrate respectively. Height of observed flame column 3 mm, SP 900. (1) Ca 20 p.p.m.; (2) Ca 20 p.p.m. + Al 15 p.p.m., both as chlorides; (3) Ca 20 p.p.m.; (4) Ca 20 p.p.m. + Al 15 p.p.m., both as nitrates.

An attempt was made to define the exact composition of the aluminates formed, by X-ray diffraction analysis of the unevaporated particles leaving the flame. The Debye–Scherrer diffractograms revealed that magnesium forms the spinel, *i.e.* $MgO \cdot Al_2O_3$. For calcium and aluminum the diffraction patterns were not distinct. This may be explained as follows: calcium and aluminum oxides form several phases of different composition, *i.e.*, $3\ CaO \cdot 5\ Al_2O_3$, $CaO \cdot Al_2O_3$, $5\ CaO \cdot 3\ Al_2O_3$ and $3\ CaO \cdot Al_2O_3$, all of which have melting points considerably lower than the temperature of the air–acetylene flame used[11]. The melted particles after leaving the flame cool quickly so that crystallization does not take place and a glassy structure results. The spinel, however, has a much higher melting point (*ca.* 2130°) which is a little above or near the flame temperature, so that the crystalline form of the particles is not disturbed.

The mechanism of the releasing effect

For the elimination of depressing effects based on the formation of involatile compounds, several methods have been proposed; the most widely used is the so-called "releasing effect"[4]. This is based on the observation, that after addition of a releasing element in sufficient amounts, the signal of the alkaline earth element in the flame in absence of the interfering element is recovered. Lanthanum[12] and strontium[13] are the releasing elements mostly used. The following mechanism of this releasing effect has been suggested[12]: the releasing element forms a less soluble compound with the interfering element and during evaporation of the spray droplets this compound crystallizes preferentially leaving the required element unbound.

The amount of the releasing element needed for a complete recovery of the analysed element can be estimated from recovery curves, which are usually plotted as the signal of the analysed element against the amount of the interfering element for different concentration levels of the releasing element. To express the recovery curves in a more general form, the signal should be plotted against the ratio of the releasing and interfering element. A logarithmic scale allows a broader concentration interval to be covered. The recovery curves were better defined for nitrates than for chlorides, calcium chloride evaporating partly before forming to calcium oxide and thus escaping the reaction with aluminum. This effect was avoided by adding citric acid; calcium citrate crystallizes more quickly than calcium chloride, and then decomposes to calcium oxide so that the formation of calcium aluminate may proceed fully. Recovery curves were therefore measured with chloride solutions after citric acid had been added to give a 0.4% final solution.

The amount of releasing element needed for a complete recovery of the analysed element depends mainly on its chemical properties, rather than on the properties of the sprayer and burner used and on the concentration level. This may be seen from Fig. 4, where the recovery curves for calcium in presence of lanthanum are plotted for different concentration levels of aluminum (30 and 100 p.p.m.) and for different sprayers. Recovery curves for strontium are identical. The ratio needed for a complete recovery seems to grow somewhat with growing size of the aerosol particles. Recovery curves for magnesium are similar (Fig. 5). For a complete recovery the ratio of lanthanum to aluminum should be between 1 and 2 for calcium and strontium and 1 for magnesium. This ratio suggests that the compound formed is lanthanum aluminate, $LaAlO_3$. An attempt was made to confirm this by X-ray diffraction analysis but as in the case of calcium aluminates, the diffractograms were hazy. Lanthanum aluminate melts at 1900° which is still some 200° below the flame temperature. Difficulties were found in obtaining the d-values for the X-ray analysis for lanthanum aluminate. For this purpose, small sticks (2 × 2 × 30 mm) of a mixture of lanthanum and aluminum oxides were pressed and then placed into an air–acetylene flame for 1 h. The d-values of the resulting phase agreed well with the calculated values for $LaAlO_3$ but not with those for the aerosol particles in the air–acetylene flame. It seems, therefore, that although its chemical composition may be identical, the phase actually formed in the flame may have some other crystallographic structure. Rare earth aluminates may have a garnet or perovskite structure but different authors disagree on the particular temperature at which these are formed[14].

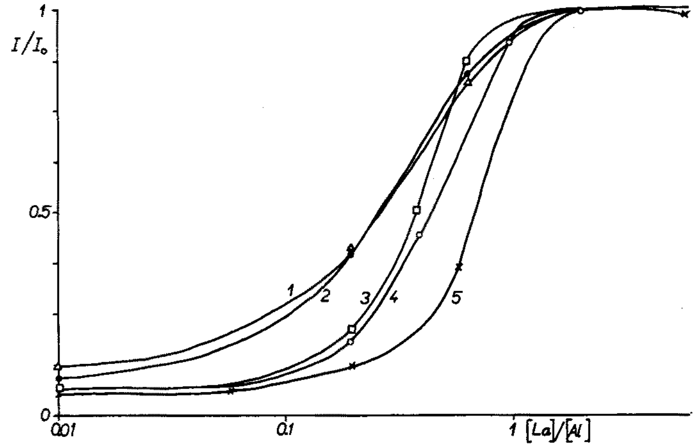

Fig. 4. Recovery curves with different sprayers of calcium for different aluminum levels. Both added as chlorides. (1) 30 p.p.m. Al, Zeiss sprayer; (2) 30 p.p.m. Al, SP 900 sprayer; (3) 100 p.p.m. Al, SP 900 sprayer; (4) 100 p.p.m. Al, Zeiss sprayer; (5) 100 p.p.m. Al, home-made sprayer. I = signal measured, I_0 = signal in absence of aluminum. Citric acid was added (0.4 % final solution) to make the recovery curves better defined.

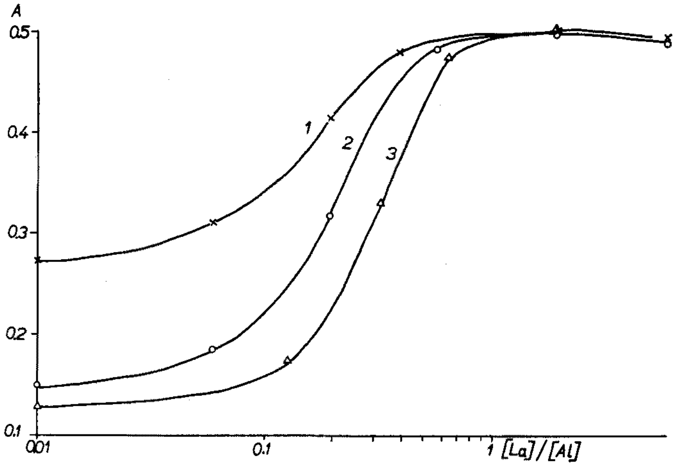

Fig. 5. Recovery curves of magnesium for different aluminum levels. Absorption measured. (1) 30 p.p.m. Al; (2) 100 p.p.m. Al; (3) 300 p.p.m. Al. Home-made sprayer, citric acid added (0.4%).

The mechanism of the effect of organic compounds

Another common approach to the elimination of the depressing effect of aluminum is the use of organic compounds. When Beckman burners are used, probably any organic compound has a positive influence[15-17], but with indirect sprayers not all of these are effective; oxine and EDTA have mostly been used.

There is little unanimity in the explanation of the mechanism of this effect. Considering the chelating properties of some of these compounds, several authors suppose that chelates are formed so that the involatile compound is not formed[7]. Some confirmation of this view based on measurements with a Beckman oxy-acetylene burner is claimed by DEBRAS-GUÉDON[18]. However, BAKER AND GARTON[3] disagree, arguing that the formation of chelates in strong acid solutions is improbable. Besides, some compounds with no chelating properties are also effective[3,19]. BAKER supposes that the organic compounds are built into the solid particles during crystallization and cause their explosive disintegration on heating in the flame. Thus, smaller particles and more complete volatilization are found.

To test this assumption, concentrated solutions (10000 p.p.m. Al + 5000 p.p.m. Mg) were sprayed, and the aerosol leaving the flame was filtered off and observed with a microscope. The mean size of the particles in presence as well as in absence of oxine was found to be essentially unchanged, their diameter being about 1 μ. This may be seen on Figs. 6a, b. It should be noted that in Fig. 6a, the particles form bigger clusters than those shown in Fig. 6b, though the size of the individual particles is about the same.

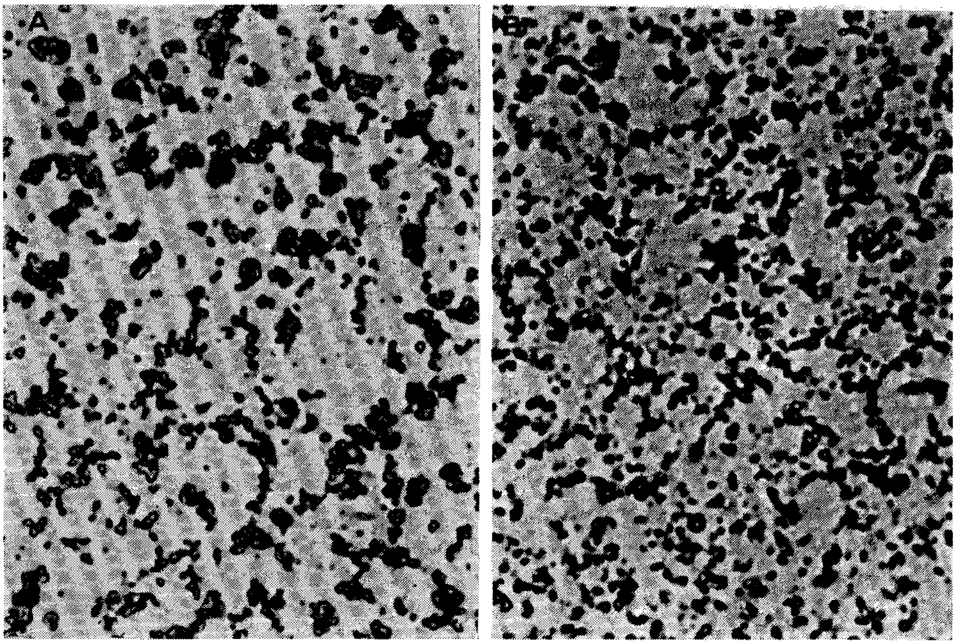

Fig. 6. Aerosol particles leaving the flame 1100 times enlarged. The sprayer and burner from the Zeiss flame photometer were used. (a) 10000 p.p.m. Al + 5000 p.p.m. Mg; (b) same in 1% oxine solution.

Nevertheless, the first explanation based on chelate formation cannot be fully accepted because, for example, urotropine without chelating properties has been found almost as effective as oxine (see Fig. 7). The following explanation is therefore suggested. As shown earlier the formation of aluminates proceeds in two stages: first the chloride must be converted to the oxide and then the oxide reacts with aluminum oxide. Oxine and other organic compounds may hinder the first reaction, *i.e.* the formation of oxides either by forming chelates during evaporation of water droplets or simply by their reducing properties after crystallization and heating of the salt particles. (It is well known that tars are formed in the thermal decomposition of oxinates.) The alkaline earth metal has then more time to evaporate before forming the involatile aluminate and a higher concentration results in the gaseous phase. An important condition is that the organic compound must be built into the particle during the crystallization so that the organic matter may directly influence the formation of the alkali earth and aluminum oxides. Therefore when cloud-chamber sprayers are used, the more volatile organic compounds are not effective.

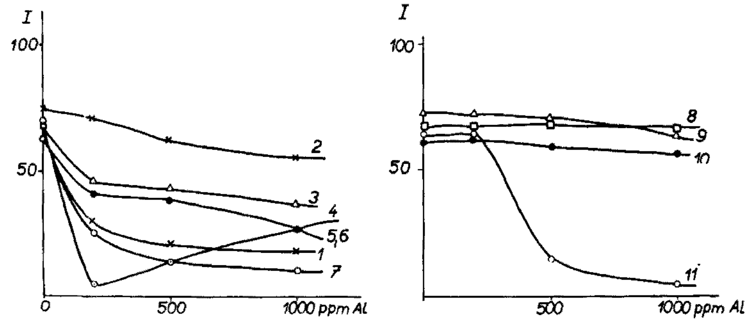

Fig. 7. The effect of aluminum on calcium chloride in presence of different compounds. (1) 10 p.p.m. Ca; (2) + 1000 p.p.m. La; (3) + 1% urotropine; (4) + 1% citric acid; (5) + 1% oxine; (6) + 1% NH$_4$Cl; (7) + 1% ammonium tartrate; (8) + 1000 p.p.m. La + 1% oxine; (9) + 1000 p.p.m. La + 1% urotropine; (10) + 1000 p.p.m. La + 1% NH$_4$Cl; (11) + 1000 p.p.m. La + 1% citric acid.

CONCLUSIONS

From the analytical point of view these observations have important consequences. It is naturally more effective to attack the interfering process in both stages by using both types of reagents simultaneously, oxine to retard the oxide formation and lanthanum to block the aluminum oxide formed. The use of lower concentrations of lanthanum for a complete release is thus made possible and requirements on the alkali earth impurities in the lanthanum compound used are diminished. Whereas 1% or even 2% lanthanum solutions are usually recommended, no more than a 0.2% solution is actually needed in a 1 % oxine solution to eliminate the effect of 390 p.p.m. aluminum (molar ratio La/Al = 2). In a work published recently Adams and Passmore used a combination of EDTA and lanthanum with similar results[20].

The formation of involatile compounds of alkaline earth metals with aluminum may proceed only if the particular elements in the aerosol particles are present as oxides. Any compound which delays the formation of oxides from the respective chlorides decreases the depressing effect of aluminum.

It has been further proved by X-ray diffraction analysis of the unevaporated particles leaving the flame, that the spinel MgO · Al$_2$O$_3$ is formed in presence of magnesium and aluminum salts in the solution sprayed. For calcium and strontium the exact composition of the compound formed could not be determined and it probably depends on the relative amounts of these elements. The compound formed with lanthanum as releasing element seems to be lanthanum aluminate, $LaAlO_3$, but this could not be proved by X-ray analysis.

SUMMARY

The depressing effect of aluminum on the signal of alkali earth metals in an acetylene–air flame with a spray chamber and the various possibilities of eliminating this interference were investigated. The importance of processes taking part in the crystalline aerosol particles before volatilization, as revealed by flame profiles is emphasized, and appropriate mechanisms for the depressing effect and its elimination are suggested.

RÉSUMÉ

Une étude est faite sur l'influence dépressive de l'aluminium sur le signal des métaux alcalino terreux dans une flamme acétylène air et les diverses possibilités d'éliminer cette interférence. On propose un mécanisme de cet effet et un moyen de l'éliminer.

ZUSAMMENFASSUNG

Die Depression des Aluminiums auf das Signal von Erdalkalimetallen in einer Azetylen–Luft-Flamme und die verschiedenen Möglichkeiten, diese Störung zu eliminieren, wurden untersucht. Es wird die Wichtigkeit dieses Prozesses hervorgehoben, der vor der Verdampfung in den kristallinen Aerosolteilchen stattfindet, wie es die Flammenprofile erkennen lassen. Ein angemessener Mechanismus dieses Effektes und seine Elimination werden vorgeschlagen.

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USE OF A CONTINUOUS SOURCE OF EXCITATION, AN ARGON–HYDROGEN–AIR FLAME, AND AN EXTENDED FLAME CELL FOR ATOMIC ABSORPTION FLAME SPECTROPHOTOMETRY

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(Received June 2nd, 1966)

Atomic absorption flame spectrophotometry using line sources of excitation is probably the most used analytical technique for trace analysis of metals. This is primarily a result of the large number of papers describing the broad application of this technique and the availability of commercial instrumentation. Even so, there are several inherent limitations to this analytical method. For example, line sources are expensive and require time to position optically, and when they are used, it is impossible to carry out rapidly qualitative as well as quantitative analyses. In addition, most commercial atomic absorption flame spectrometers are quite limited as to choice of fuel and oxidant because of burner design. Several commercial instruments are restricted to just flame absorption analyses and cannot be conveniently used for flame emission or fluorescence measurements.

WALSH[1] considered the problems involved in using a spectral continuum for atomic absorption studies in his original paper and concluded that it would be more feasible to use a line source of radiation. GIBSON, GROSSMAN AND COOKE[2] first demonstrated the feasibility of using a spectral continuum for performing qualitative and quantitative analyses. Recently IVANOV AND KOZYREVA[3] and especially FASSEL *et al.*[4,5] have demonstrated that excellent sensitivities are possible when using a continuous source.

This investigation was carried out to develop an experimental system which would have maximum versatility without significant loss in sensitivity of measurement. Experimental results indicate that the same experimental system is useful for a variety of elements with little or no loss in sensitivity compared to conventional atomic absorption flame spectrometry in which line sources are used. The theoretical implications of using a spectral continuum of radiation and the factors involved in defining the limit of detectability have been discussed in the accompanying paper[6].

EXPERIMENTAL

Apparatus

The instrumental set-up used to make the flame absorption measurements is shown in schematic form in Fig. 1. The specific components used in the experimental set-up and operating conditions for measurements are given in Table I.

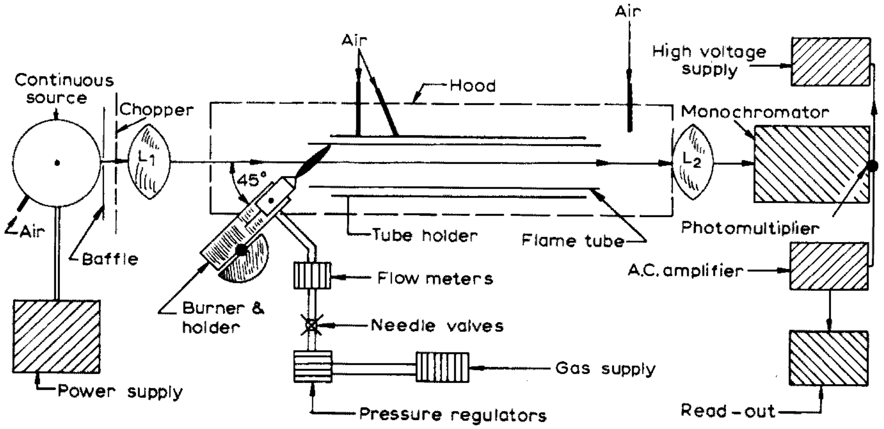

Fig. 1. Experimental set-up.

TABLE I

SPECIFIC COMPONENTS OF EXPERIMENTAL SYSTEM AND OPERATING CONDITIONS

(1) Spectral continua.	Xenon arc, 150 W (Englehard, Hanovia, Newark, N. J.) powered by a regulated a.c. supply (Sola Electric Co., Chicago, Ill.) used for range of 2700–6000 Å. The jacket surrounding the xenon lamp has a connector for cooling air and a baffle hole of 5/32″ diameter. Tungsten filament lamp (No. 2305, Beckman Instruments Inc., Fullerton, Calif.) powered by a 6-V storage battery and used for range of 3500–8500 Å. A baffle with a 5/32″ hole was placed in front of the tungsten lamp.
(2) Optics.	Single pass, chopped at 320 c/s. Chopper consists of a disc with 11 equally spaced holes rotated by an 1800 rev/min synchronous motor (Bodine Electric Co., Chicago, Ill.). L_1 and L_2 are quartz lenses. L_1 is a collimating lens, 8.0 cm focal length. L_2 is a focusing lens, 5.0 cm focal length. Flame tube is thick-walled Vycor, 12 inches long with a 1.6 cm O.D. and 1.0 cm I.D. (Englehard Industries Inc., Hillside, N. J.). Tube was held in place by a laboratory clamp. Radiation passing down the tube underwent a series of multiple reflections[8]. The tube holder was fitted with connectors to direct air at the flame tube to prevent burnout and to extend the lifetime of the flame tube. A small hood was positioned over the flame tube and holder to remove flame gases and to cool the unit.
(3) Monochromator.	Jarrell-Ash, Model 82000, 0.5-m Ebert Mount, grating spectrometer (Jarrell-Ash Co., Waltham, Mass.). Grating is ruled for 1250 lines/mm and is blazed at 5000 Å. Reciprocal linear dispersion is 16 Å/mm in the first order. Variable slits were used; however, all measurements were made using a 10-μ slit width. This corresponds to a theoretical spectral bandwidth of 0.16 Å in the first order. Measured minimum spectral bandwidth was 0.25 Å.
(4) Detector-power supply.	EMI 9558 QB photomultiplier (1650–9000 Å). Regulated d.c. power supply (No. 418 A, Fluke Mfg. Co., Seattle, Wash.).
(5) Amplifier-readout electronics.	A.C. photomultiplier output signal was fed into an O.R.N.L. Model No. 7 a.c.[7] amplifier tuned to 320 c/s. The plate and filament voltages were taken from a dual power supply (No. R 100 B, Philbrick Researches, Boston, Mass.). The a.c. signal was rectified and the d.c. signal was recorded on a potentiometric recorder (Model TR, E. H. Sargent and Co., Chicago, Ill.). The 12.5-mV scale was used at all times except when near the limit of detectability for a particular element. At or near the limit of detectability, the scale was expanded by proper adjustment of the zero suppress and by using a lower scale setting (5.0, 2.5 or 1.25 mV) on the recorder.

TABLE I *(continued)*

(6) Gas pressure and flow regulation.	Tank pressure is reduced by appropriate two stage-high pressure regulators (The Matheson Co., Inc., East Rutherford, N. J.). The gas flow is then further regulated by a Beckman High-Precision regulation unit (No. 9220, Beckman Industries Inc., Fullerton, Calif.). The resultant flow is monitored by rotameters (No. 4-15-2 Ace Glass Co., Inc., Vineland, N. J.). The flow rate of aspirating gas was 2.25 l/min for argon by 2.75 l/min for air. The flow rate of hydrogen was optimized for each element and is given in Table II.
(7) Aspirator-burner.	Total-consumption type. Medium bore (No. 4020, Beckman Instruments Inc., Fullerton, Calif.) burner was mounted at an angle of 45° to the optical axis of the quartz tube, and the burner tip was placed about 0.5 cm away from the end of the quartz tube. For the aspirating gas flow rate, the solution flow rate was about 1.0 ml/min. The capillary length was extended by means of Teflon tubing.

Solutions

Stock solutions of 1000 p.p.m. for each element were prepared by dissolving an appropriate salt in aqueous solution or the metal in acidified-aqueous solution. More dilute solutions were made by successive dilution of this stock solution.

Procedure

The wavelength used for the atomic absorption measurements of each element was selected by aspirating a 50-p.p.m. solution of the element of interest and then manually scanning to locate the wavelength of maximum absorption. Scanning the wavelength range is useful because the optimum absorption wavelength can be determined, if more than one wavelength is available (*e.g.*, the transition metals) and because the background signal adjacent to the wavelength of interest can be measured. In addition, the presence of contaminating elements in the solutions can be determined.

The flame tube was flushed after each measurement by continuously aspirating water. This was necessary to extend the lifetime of the flame tube by preventing burn out and salt fusion, and to reduce the noise on the background signal. Periodic flushing of the tube with dilute nitric acid minimized the decrease in reflectivity of the flame tube due to salt fusion.

Additional discussion of the experimental technique and problems encountered in using the flame tube may be found in articles by FUWA AND VALLEE[8] and KOIRTYOHANN AND FELDMAN[9].

RESULTS

Limits of detectability for 21 elements measured using the experimental technique above are given in Table II. The limit of detectability[10] is defined as that solution concentration resulting in a signal-to-noise ratio of 2.0. The limits of detectability given in Table II represent an average of 9 determinations having less than a 50% relative standard deviation. These values are the lowest obtainable using the experimental setup described above and various combinations of fuel and oxidant, *i.e.*, various combinations of C_2H_2, H_2, O_2, and air as well as argon.

TABLE II

EXPERIMENTAL CONDITIONS AND LIMITS OF DETECTION OBTAINED FOR 21 ELEMENTS

Element	*Wavelength (Å)*	*H_2 flow rate (l/min)*	*Phototube voltage (V)*	*Limits of detectability (p.p.m.)*		
				Continuous source		*Line source*
				This work	FASSEL *et al.*[4]	SLAVIN[14]
Li^{b}	6707	4.5^{f}	1360	0.01	0.004	0.005
Na^{a}	5890	4.0^{f}	1300	0.02	0.03	0.005
K^{a}	7665	4.5^{f}	1500	0.07	0.03	0.005
Rb^{a}	7800	5.3^{f}	1500	0.01	0.04	0.02
Ag^{a}	3281	4.2	1060	0.01	0.2	0.02
Mg^{a}	2852	5.6	1300	0.007	0.01	0.003
Ca^{b}	4227	7.5	970	0.09	0.03	0.01
Sr^{b}	4607	11.5	1020	0.02	0.06	0.02
Ba^{b}	5535	13.0	1000	0.1	0.9	1.0
Cu^{a}	3247	13.0	1140	0.02	0.05	0.005
Mn^{e}	2798	8.5	1100	0.01	0.07	0.01
	4032	8.5	1100	0.5	—	—
Ni^{c}	3414	6.2	1140	0.5	0.7	0.05
	4032	6.2	1140	0.1	—	—
Cr^{d}	3579	7.7	1130	0.2	0.2	0.01
Co^{b}	3526	4.8	1100	0.4	3	0.15
Fe^{c}	3021	4.8	1200	0.04	1	0.05
Bi^{c}	3067	4.5	1000	0.07	4	0.2
Sn^{c}	2863	4.6	1140	0.02	6	2.0
Pb^{b}	2833	4.6	1100	0.2	2	0.15
Ga^{c}	2874	8.4	1100	0.5	2	1.0
In^{b}	3040	5.8	1170	0.04	0.2	0.5
Tl^{c}	3775	4.6	1100	0.02	0.6	0.2

[a] As the chloride salt. [b] As the nitrate salt. [c] Solutions were prepared by dissolving the pure metal in a minimum amount of concentrated hydrochloric acid. [d] As the dichromate salt. [e] Prepared by dissolving MnO_2 in hydrochloric acid. [f] Limits of detectability using air /H_2 flame.

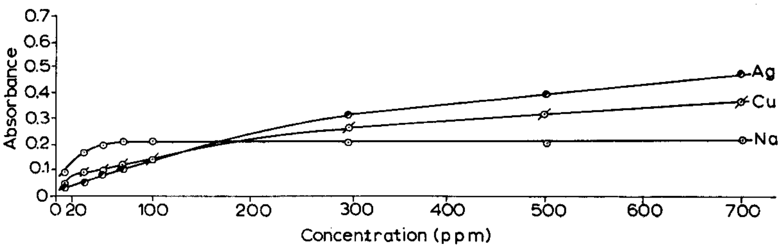

Fig. 2. Analytical absorbance curves for 3 elements using a continuous source.

Relative standard deviations were calculated on the basis of 9 runs for 100 p.p.m. and at a 10-fold concentration higher than that determined for the limit of detectability as well as at the limit of detectability. For concentrations 10-fold higher than the limit of detectability, the relative standard deviation was never larger than 1.0% for all elements run, whereas at 100 p.p.m., the relative standard deviation was between 2.0 and 8.5% depending upon the particular element. In Fig. 2, typical working curves for 3 elements are given. In general, the shape of the absorbance *vs.* concentration working curve when a spectral continuum is used as a source of radiation is characterized by a linear portion in the low concentration range, which gradually curves off at higher concentrations which is to be expected[6]. From Fig. 2, it can be seen that the working curve for silver is linear from about 0.01 p.p.m. to about 100 p.p.m., whereas the copper and sodium curves are linear from about 0.02 to about 30 p.p.m. All other elements give curves similar to those of sodium and copper.

DISCUSSION

A spectral continuum as a source of radiation certainly eliminates many of the restrictions placed on atomic absorption by the use of line sources of radiation. In addition, line sources often are of low intensity, low stability, and short lifetime for many elements, as well as expensive and time-consuming if many lamps must be used for analysis.

One of the major disadvantages of the total-consumption aspirator burner for atomic absorption studies is the very short absorption path length of the flame even under very fuel-rich conditions. Therefore, the flame tube was used to extend the effective path length (actually the residence time of atoms in the light path) of the flame gases. FUWA AND VALLEE[8] were the first to suggest the use of the flame tube for atomic absorption analyses; however, they used line sources of radiation. Later KOIRTYOHANN AND FELDMAN[9] and more recently KOIRTYOHANN AND PICKETT[11,12] have determined limits of detectability and discussed possible source of spectral interferences using the flame tube. It is interesting to note that although their applications involved the use of a line source of radiation, a spectral continuum source was suggested as a means of correcting for spectral interferences.

The flame tube has the additional advantage that misalignment of the aspirator-burner or incorrect positioning of the flame in the light path is not as critical as alignment of the line source and acetylene–air flame used with most chamber type aspirator-burners. Of course, alignment of the flame tube in the light path is critical.

The argon–hydrogen–entrained air (Ar/H_2–E.A.) flame was used in these studies because of the success of this flame in atomic fluorescence[13] and atomic emission[14] studies. The total-consumption aspirator-burner combined with the argon–hydrogen–entrained air flame[13] and the flame tube is an efficient method of producing atoms. This is evident from the data in Table II. The good sensitivity of the Ar/H_2–E.A. flame is a result of two factors, namely: the Ar/H_2–E.A. flame has a very low background which results in greater sensitivity[10,13]; and the total-consumption aspirator–burner in conjunction with the Ar/H_2–E.A. flame and the flame tube results in a greater efficiency of atomization than is obtained for most other aspirator-burner–flame systems. The longer residence of atoms in the flame tube and the reducing characteristics of the flame gases decrease compound formation and therefore increase the efficiency of atomization.

The requirements of the monochromator when using a spectral continuum of radiation are, of course, more critical than when a line source of radiation is used. For the case where the line source is used, WALSH[1] concluded that a low-resolution monochromator capable of isolating the resonance line from the source was all that was required. For the case where a spectral continuum is used, WINEFORDNER[16] has shown that as the spectral bandwidth of the monochromator approaches the absorption line width of atoms in the flame, the sensitivity of measurement will increase almost linearly with decrease in the spectral bandwidth. GIBSON, GROSSMAN AND COOKE[2], indicated that a medium-resolution, large-aperture, bench-sized monochromator combined with a scale expansion technique should give good sensitivity. This result has been recently confirmed by FASSEL *et al.*[5]. Our experimental system also consists of a medium-resolution monochromator and an electronic system capable of a 10-fold scale expansion. With the experimental system described in this paper, the limits of detectability are comparable to or greater than the best values listed in the literature for a line source–acetylene–air flame system and the values listed by FASSEL *et al.*[4] for a continuous source–fuel-rich acetylene–oxygen system (see Table II). This certainly indicates that the spectral continuum (in conjunction with the flame tube and the Ar/H_2–E.A. flame) as a source of excitation should be competitive to the use of the line source and a typical air–acetylene flame and chamber-type aspirator-burner measurement system.

Owing to the curvature of the working curves at high concentrations, a working curve must be prepared before a quantitative measurement is made. RUBESKA AND SVOBODA[17] and DE GALAN, MCGEE AND WINEFORDNER[6] discuss the factors causing bending of working curves in atomic absorption flame spectrophotometry. FASSEL *et al.*[5] discuss the necessary corrections which must be made in the preparation of a working curve. Although experimental working curves are curved at high concentrations, they are reproducible over a period of months and therefore are very useful for quantitative measurements.

The qualitative aspect of atomic absorption analyses has been neglected because of the restrictions normally placed on the measurement system by the use of line sources. In these studies, a qualitative investigation and quantitative estimate of the sensitivity of the major atomic absorption lines of each element was used to determine the absorption lines for measurement.

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SUMMARY

A continuous source of excitation in conjunction with an argon–hydrogen-entrained air flame, an extended flame cell, a medium-dispersion monochromator and a typical detection system is shown to give good sensitivities for the atomic absorption flame spectrophotometric measurement of 21 elements. Useful working curves over a 100-fold concentration range are obtained for each of the 21 elements using the simple experimental system. The advantages gained with this system are discussed.

RÉSUMÉ

Les auteurs ont obtenu de bonnes sensibilités lors des mesures spectrophotométriques par absorption atomique de 21 éléments, à l'aide d'une source d'excitation continue avec flamme argon–hydrogène–air, d'un monochromateur de dispersion moyenne et d'un système de détection typique. Une discussion est donnée sur les avantages de ce système.

ZUSAMMENFASSUNG

Bei der Flammenabsorptionsanalyse wurden gute Empfindlichkeiten für 21 Elemente erhalten bei Verwendung einer kontinuierlichen Anregung in Verbindung mit einer Argon–Wasserstoff–Luft-Flamme, einer ausgedehnten Flammenzelle, eines Monochromators mit mittlerer Dispersion und eines typischen Detektorsystems. Es wurden brauchbare Eichkurven für einen Bereich von zwei Zehnerpotenzen für jedes der 21 Elemente gefunden. Die Vorteile dieses Systems werden diskutiert.

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COMPARISON OF LINE AND CONTINUOUS SOURCES IN ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Several years after the introduction of atomic absorption spectrophotometry in 1955 by WALSH[1], GIBSON, GROSSMAN AND COOKE[2] first indicated the possibility of using a continuous light source. Since then, practical application of a continuous source has been described both with a high-resolution monochromator[3] and with a medium-dispersion instrument[4]. Using a special flame and a long quartz absorption tube, McGEE AND WINEFORDNER[5] obtained detection limits comparable to those reported for a line source.

The continuous source offers several important advantages: possibility of qualitative analysis, simplicity of background correction[6], gain in analysis time; moreover, its low price easily compensates for the additional cost of a higher resolution monochromator.

The major objection to replacing the popular hollow-cathode discharge tubes by a single continuous source appears to be the opinion that line sources yield much larger absorption signals and much lower detection limits. Therefore, a quantitative investigation of the signals obtained in both cases and a critical discussion of the factors influencing the signals are presented in this paper.

THEORY

In order to indicate the similarities and the differences in the use of a continuous source and a line source in atomic absorption spectrometry, it is assumed that the same basic equipment consisting of a flame cell, a monochromator and an electrometer-readout system is used in both cases. Consequently, the instrumental proportionality factor, K, relating readout-voltage to intensity of radiation reaching the entrance slit of the monochromator, will be the same in both cases.

A monochromator is used capable of isolating a single line but not capable of resolving the spectral line profile. This means that the spectral bandwidth of the monochromator, s, is considerably larger than the absorption line width, $\Delta\lambda_A$. In turn, the absorption line width is assumed to be larger than the width of the line emitted by the line source, $\Delta\lambda_S$.

Atomic absorption measurement with a line source

The photodetector signal due to radiation emitted by the line source passing through the flame gases with only blank solution being aspirated is given by

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[*] On leave from University of Amsterdam, The Netherlands.

$$I_1{}^0 = K\int_{\Delta\lambda_S} J_\lambda{}^0 \mathrm{d}\lambda \tag{1}$$

where J is the intensity per unit of wavelength.

The signal from the radiation passing through the flame with sample solution being aspirated is given by

$$I_1 = K\int_{\Delta\lambda_S} J_\lambda{}^0 \exp(-k_\lambda L)\,\mathrm{d}\lambda \tag{2}$$

where L is the path length in the flame.

In general, the atomic absorption coefficient, k_λ, is a complex function of the wavelength and is described by the following set of formulae[7]:

$$k_\lambda = k_0\,\delta(a,v) \tag{3}$$

$$k_0 = \frac{\sqrt{4\pi \ln 2}\; e^2 \lambda_0{}^2 N f}{m\,c^2\,\Delta\lambda_D} \tag{4}$$

$$\Delta\lambda_D = \frac{\lambda_0}{c}\sqrt{\frac{8\,RT\ln 2}{M}} \tag{5}$$

$$\delta(a,v) = \frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-y^2)\,\mathrm{d}y}{a^2+(v-y)^2} \tag{6}$$

where e and m are charge and mass of the electron, c the velocity of light, λ_0 the wavelength at the line center, f the oscillator strength, N the concentration of absorbing atoms in the flame, T the flame temperature, R the gas constant, M the atomic mass, $\Delta\lambda_D$ the Doppler half-width of the absorption line, a the damping constant (given by $a = (\ln 2)^{\frac{1}{2}}\Delta\lambda_C/\Delta\lambda_D$), $\Delta\lambda_C$ the collisional half-width of the absorption line, and v is equal to $(4\ln 2)^{\frac{1}{2}}\,(\lambda-\lambda_0)/\Delta\lambda_D$.

The function $\delta(a,v)$ describes the variation of k_λ over the entire *absorption* line. However, the integration in eqn. (2) extends over the emission line width, $\Delta\lambda_S$, only, which is generally much smaller than the absorption line width. This restricts the range of v to an upper limit of about $\Delta\lambda_S/\Delta\lambda_A$. From the data presented in Table I, it is seen that the relative decrease of k_λ with increasing value of v is rather small if the damping constant, a, exceeds a value of 0.5 (see below). In that case, eqn. (2) can be approximated as

$$I_1 = K\mathrm{e}^{-\bar{k}L}\int_{\Delta\lambda_S} J_\lambda{}^0 \mathrm{d}\lambda = I_1{}^0\mathrm{e}^{-\bar{k}L} \tag{7}$$

where

$$\bar{k} = k_0\delta(a,\bar{v}) \tag{8}$$

represents the average absorption coefficient over the source line width, $\Delta\lambda_S$, and $\bar{v}$ is an average over the range from zero to $\Delta\lambda_S/\Delta\lambda_A$.

Consequently, the absorbance is given by

$$A_1 = \ln(I_1{}^0/I_1) = \bar{k}\,L, \tag{9}$$

and for very small concentrations, when $\bar{k}L \ll 1$, the fraction of the intensity absorbed in the flame is given by

$$\alpha_1 = \frac{I_1^0 - I_1}{I_1^0} = 1 - e^{-\bar{k}L} = \bar{k}L = \frac{\sqrt{4\pi \ln 2}\, e^2\lambda_0^2\, NfL\, \delta(a,\bar{v})}{mc^2\, \Delta\lambda_D} \tag{10}$$

The minimum detectable atomic concentration, $N_{\min}$, is defined as the concentration that produces a signal equal to twice the noise. When a line source is used in atomic absorption spectrometry, the main contribution to the noise is the variation in the source intensity, χ. According to WINEFORDNER AND VICKERS[8], the detection limit is then found from the relation

$$\alpha_1(N_{\min}) = 2\chi_1 \sqrt{\Delta f} \tag{11}$$

where Δf is the frequency bandwidth of the electrometer-readout system. Substitution of eqn. (10) into eqn. (11) yields

$$N_{\min,1} = \frac{mc^2\, \Delta\lambda_D \chi_1 \sqrt{\Delta f}}{\sqrt{\pi \ln 2}\, e^2\lambda_0^2 fL\, \delta(a,\bar{v})} \tag{12}$$

Atomic absorption measurement with a continuous source

With a line source, the wavelength region of interest is determined by the width of the source line, whereas the decisive parameter in the case of a continuous source is the spectral bandwidth of the monochromator, s; over this small range, the intensity of the source is essentially constant. Therefore, the blank photodetector signal is given by

$$I_c^0 = K \int_s J_\lambda^0 d\lambda = K J_{\lambda_0}^0 s \tag{13}$$

and for the photodetector signal due to radiation passing through the flame with sample solution being aspirated, we have

$$I_c = K \int_s J_\lambda^0 \exp(-k_\lambda L)\, d\lambda = K J_{\lambda_0}^0 \int_0^\infty \exp(-k_\lambda L)\, d\lambda \tag{14}$$

where the integration limits are 0 and ∞ because the spectral bandwidth is assumed to be much larger than the width of the absorption line. The fraction of the intensity absorbed in the flame is given by

$$\alpha_c = \frac{I_c^0 - I_c}{I_c^0} = \frac{\int_0^\infty (1 - \exp(-k_\lambda L) d\lambda}{s} = \frac{A_T}{s} \tag{15}$$

where A_T is known as the total absorption[7]. Curves representing A_T as a function of the concentration N (curves of growth) depend on the value of the damping constant, a[9,10]. At very high concentrations, A_T is proportional to $N^{\frac{1}{2}}$; at very low concentrations, where $k_\lambda L \ll 1$ at any position in the absorption line, eqn. (15) yields

$$\alpha_c = \frac{\int_0^\infty k_\lambda L\, d\lambda}{s} = \frac{\pi e^2\lambda_0^2\, NfL}{mc^2 s} \tag{16}$$

which is independent of the absorption line profile.

The general expression for the absorbance, A, is in this case

$$A_c = \ln(I_c{}^0/I_c) = -\ln(1 - A_T/s) \tag{17}$$

An expression for the minimum detectable concentration is found in the same way as for the line source, if again the variation in source intensity is assumed to constitute the main contribution to the noise

$$N_{\min,c} = \frac{2\, mc^2 s \chi_c \sqrt{\Delta f}}{\pi e^2 \lambda_0{}^2 fL} \tag{18}$$

where the frequency bandwidth, Δf, is the same as in eqn. (12).

DISCUSSION

Working curves

Working curves in absorption spectrometry are usually presented as a plot of absorbance, A, *versus* the solution concentration of the element, C. It follows from eqns. (9) and (10) that if a line source is used in atomic absorption spectrometry, such a plot should produce a straight line as long as the concentration of an element in the flame is proportional to its concentration in solution. When a very narrow line source is used (*i.e.* $\Delta\lambda_S \ll \Delta\lambda_A$, $\bar{v} \approx 0$), this straight line should extend over an extremely large concentration range; namely, up to the point where the resonance broadening causes the damping constant to change[7], which is in the region of molar solutions. In practice, however, the linear range of the working curve is restricted by chemical interferences in the flame (ionization and compound formation of the atom in concern) and by a nonlinear relation between flame gas concentration, N, and solution concentration, C, due to variation in aspiration efficiency[11]. Sloping off of the working curve occurs also if the source line width is not negligible compared to the absorption line width, since in that case the approximation of eqn. (7) is no longer valid.

If a continuous source is used in atomic absorption spectrometry, the absorbance is a complicated function of the concentration of the element in the flame. According to eqn. (17), the absorbance is proportional to the total absorption, A_T, only for small values of the ratio A_T/s. On the other hand, the fraction of the intensity absorbed in the flame, α_c, is always proportional to the total absorption. Even in this case, however, the linear portion of the working curve is restricted to the linear portion of the curve of growth (A_T *versus* N)[9,10]. The examples presented in Fig. 1 indicate that the working curves slope off when more than 10% of the radiation is absorbed in the flame. At lower values of the relative absorption linear expansion of eqn. (17) is perfectly valid. Therefore, a similar linear range is obtained for a plot of either absorbance or relative absorption *versus* concentration.

The working curves shown in Fig. 1 for a line source extend linearly over an additional decade towards higher concentrations. Therefore, curvature of the working curves obtained with a continuous source constitutes no disadvantage, if with proper scale expansion, atomic absorption spectrometry is used for the determination of low concentrations.

Comparison of signals

If the same *low* atomic concentration is measured with a line source and a continuous source, respectively, the ratio of the fractions of the intensity absorbed (or the ratio of the absorbances) is found from eqns. (10) and (16) to be

$$R_A = \frac{\alpha_l}{\alpha_c} = \sqrt{\frac{4\ln 2}{\pi}}\,\frac{s\,\delta(a,\bar{v})}{\Delta\lambda_D} \qquad (19)$$

The decisive factor in this equation is the ratio of the spectral bandwidth and the Doppler half-width of the absorption line. For an element of atomic weight 50, the Doppler half-width at 2000°K varies from 0.01 Å at 2000 Å to 0.04 Å at 8000 Å. A spectral bandwidth of the same order of magnitude can be obtained only with a high-resolution monochromator. For example, a large grating monochromator with second order reciprocal linear dispersion of 2 Å/mm and a minimum slit width of 10 μ yields a spectral bandwidth of 0.02 Å. In this case, the signal obtained with a continuous source is generally superior to that of the line source, since the factor $\delta(a,\bar{v})$ is smaller than one (see below).

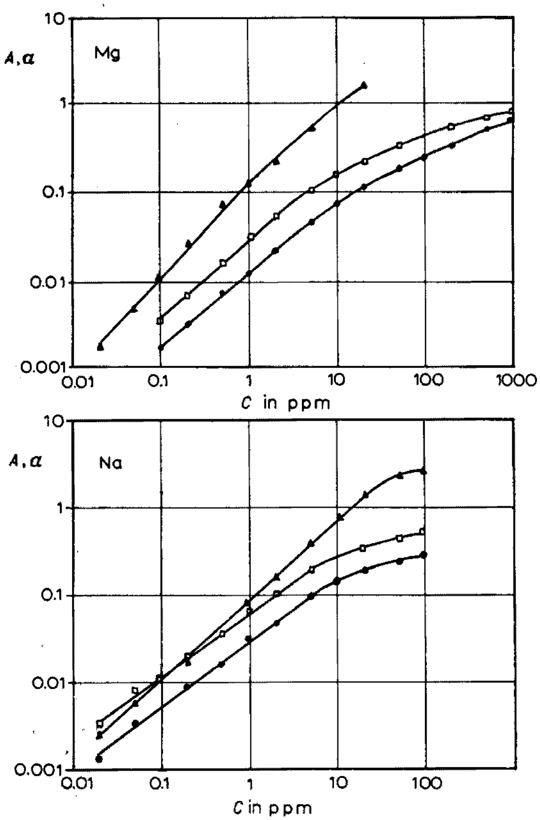

Fig. 1. Working curves in atomic absorption spectrophotometry. ● Absorbance *versus* concentration (continuous source); □ fraction absorbed *versus* concentration (continuous source); ▲ absorbance *versus* concentration (line source).

If, on the other hand, the minimum spectral bandwidth is several Å, application of a continuous source should not be attempted. Although with appropriate scale expansion fairly low concentrations can still be detected, eqn. (19) clearly shows that a gain of about two orders of magnitude can be obtained with a line source.

However, a better resolution than is offered by a low-dispersion monochromator is often desirable in atomic absorption spectrophotometry. The low intensity of many hollow-cathode discharge tubes necessitates the use of fairly large slit widths in order to detect the radiation at all (the photodetector signal is proportional to the slit width[8]). In determining elements with complicated spectra, a spectral bandwidth smaller than 1 Å is often needed for complete isolation of the analysis line. Improved sensitivity and better linearity of the working curve with decreasing spectral bandwidth have been reported in the analysis of lead[12], which element possesses a relatively simple spectrum. For this reason, it is unfortunate that low-dispersion monochromators are often used in commercial atomic absorption instruments.

A medium-dispersion monochromator, such as the 0.5-m Jarrell-Ash grating monochromator, is capable of a minimum spectral bandwidth of 0.2 Å. This is sufficient to isolate even close lying lines. Now, the advantage of using a line source is reduced to about a factor of 10, even if $\delta(a,\bar{v})$ has its maximum value of unity.

The actual value of $\delta(a,\bar{v})$ is smaller than unity because of the finite width of the source line and because of collisional broadening of the absorption line. Measurements made by YASUDA[13] show that the half-width of hollow-cathode lines is of the order of 0.01 Å, which is comparable to the Doppler half-width of many absorption lines. The data in Table I show that for a range of v from zero to unity, the decrease of $\delta(a,v)$ is quite large if the damping constant is small. For a damping constant equal to unity, the relative decrease of $\delta(a,v)$ due to the finite width of the source line amounts to about 10%.

TABLE I

VALUES FOR $\delta(a,v)$ AFTER YOUNG[16]

v	a					
	0	*0.5*	*1.0*	*2.0*	*5.0*	*10.0*
0	1.00	0.61	0.42	0.26	0.11	0.057
0.2	0.96	0.60	0.42	0.25	0.11	0.057
0.4	0.85	0.56	0.40	0.25	0.11	0.057
0.6	0.70	0.50	0.38	0.24	0.11	0.057
0.8	0.52	0.43	0.34	0.23	0.11	0.056
1.0	0.37	0.35	0.30	0.22	0.11	0.056

A damping constant equal to zero indicates that the absorption line profile is determined by Doppler broadening only. According to eqn. (16), the integral of the absorption coefficient over the complete absorption line is independent of broadening parameters. Consequently, any additional broadening of the absorption line must result in a decrease of the peak value of the absorption coefficient. This decrease of the absorption coefficient with increasing value of a is evident from the data in Table I.

Unfortunately, the value of the damping constant in a particular case is by no means certain. Experimental data show a wide divergence[9] and theoretical calculations can be given to an order of magnitude only[14]. The most probable range of a in flames is between 0.5 and 2.0[14,15]. In combination with an approximate value of 0.5 for $\bar{v}$, this yields $\delta(a,\bar{v})$-values ranging from 0.5 to 0.2 Substitution into eqn. (19) yields a corresponding reduction of the gain, R_A, of the line source over the continuous source.

This is confirmed by experimentally measured values of the gain, R_A, presented in Table II. For the resonance lines of a few elements, the absorption produced by the same low solution concentration in an acetylene/air flame (chamber-type aspirator-burner, Perkin-Elmer Corp., Norwalk, Conn.) was measured with both a continuous source (150 W Xenon arc) and with narrow line sources (hollow-cathode discharge tubes and Osram lamps run at the lowest possible currents). The minimum spectral bandwidth of a 0.5-m grating monochromator (Jarrell-Ash Co., Waltham, Mass.) was measured to be 0.20 Å. From eqn. (19), the maximum possible gain was calculated by taking $\delta(a,\bar{v}) = 1$. The experimental values of the gain factor are significantly lower than these calculated maximum values, indicating the importance of the factor $\delta(a,\bar{v})$.

TABLE II

COMPARISON OF LINE SOURCE AND CONTINUOUS SOURCE

Element and line	$\Delta\lambda_D$ *(Å)*	$(R_A)_{max}$[a]	$(R_A)_{exp}$	$(R_L)_{exp}$	$\delta(a,\bar{v})$[b]	a[c]
Na 5890	0.047	4.0	2.3	1	0.6	0.3
K 4404	0.020	9.4	3.4	2	0.35	1.2
Mg 2852	0.018	10.2	7.0	0.2	0.7	0.1
Ca 4226	0.022	8.7	4.2	1	0.5	0.6
Sr 4607	0.016	11.9	4.7	1	0.4	1.0
Ba 5535	0.015	12.4	4.	—	0.3	1.5
Cd 2288	0.0069	27.	2.	—	0.08	7.
Zn 2139	0.0085	22.	7.	—	0.3	1.5

[a] Calculated from eqn. (19) assuming $\delta(a,\bar{v}) = 1$ and $s = 0.2$ Å.

[b] Calculated as the ratio $(R_A)_{exp}/(R_A)_{max}$.

[c] Taken from Table I from calculated value of $\delta(a,\bar{v})$ assuming $\bar{v} = 0.5$.

It should be evident that a simple and quick method of measuring the a-parameter in flames could be based upon a comparison between the absorption signals obtained with a continuous source and a line source, respectively. A value for $\delta(a,\bar{v})$ can be derived from the ratio of the experimentally measured gain and the calculated maximum gain; this then yields a value for a. To the tentative data in Table II, no better accuracy can be attributed than a factor two, but with some refinements (the width of the source line should be known approximately) accuracies of 10% could be reached. It is to be noted that this method is not based on the emission of the element in the flame and thus can be applied to elements that do not emit in flames. Therefore, it provides a valuable alternative to the methods based upon the curve of growth[10,15].

Comparison of detection limits

From eqns. (12) and (18), the ratio of the minimum detectable concentrations for a line source and a continuous source is found to be

$$R_L = \frac{N_{\min,l}}{N_{\min,c}} = \sqrt{\frac{\pi}{4\ln 2}}\,\frac{\Delta\lambda_D}{s\,\delta(a,\bar{v})}\,\frac{\chi_l}{\chi_c} = \frac{R_N}{R_A} \tag{20}$$

which is equal to the ratio of the noise ratio, R_N, and the signal ratio, R_A. In general, R_N need not be restricted to the ratio of the source noises, but actually should include all noise contributions of a particular arrangement. Equation (20) shows that a large value for the signal ratio does not necessarily mean that a lower limit of detection is obtained with a line source; the gain in signal can be offset by a decrease in stability of the source. For example, from the curves shown in Fig. 1 for sodium, it is seen that the absorbance measured with a line source is twice the value measured with a continuous source, so $R_A = 2$. However, the flicker in the sodium lamp is also twice as large as the flicker in the xenon arc, so that the limit of detection is about 0.02 p.p.m. in both cases.

From the experimental values of the ratio of the limits of detection, R_L, presented in Table II, it is seen that a similar compensation (*cf.* sodium) occurs in the case of calcium and strontium, where detection limits of 0.5 p.p.m. were found with both sources; here the signal ratio is as large as 4.

On the other hand, in the determination of magnesium the variation in background absorption of the flame turned out to be the main source of noise. Here the improved stability of the xenon arc over the magnesium hollow-cathode discharge tube is of little value; the signal ratio is 7 and the ratio of the limits of detection is 0.2 in favour of the line source.

Definite conclusions about the relative limits of detection can only be drawn, when more information is available on noise levels in hollow-cathode discharge tubes and continuous sources. It has been shown, however, that with a monochromator capable of a spectral bandwidth $s \leqslant 0.2$ Å, the absorption signal measured with a continuous source is not much smaller than that measured with a line source. In addition, of course, the continuous source is superior to the line source in all other aspects.

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SUMMARY

Expressions are given for the absorption signal (absorbance or fraction absorbed) in atomic absorption spectrophotometry with a line source and a continuous source, respectively. A theoretical and experimental comparison is made between the shape of the working curves, the magnitude of the signals, and the limits of detection in both cases. The significance of the spectral bandwidth of the monochromator and the absorption line profile is discussed. With a good medium-dispersion monochromator, a continuous source offers several distinct advantages and yields detection limits which are approximately the same as those obtained with a hollow-cathode discharge tube.

RÉSUMÉ

Des expressions sont données pour le signal d'absorption (absorption ou fraction absorbée) en spectrophotométrie par absorption atomique, avec une source de ligne et une source continue, respectivement. Une comparaison théorique et expérimentale a été faite. Avec un bon monochromateur, une source continue présente de nombreux avantages et donne des limites de détection qui sont approximativement les mêmes que celles obtenues avec un tube de décharge à cathode creuse.

ZUSAMMENFASSUNG

Es werden Gleichungen für die Absorption bei der Flammenabsorptionsphotometrie angegeben und zwar für einen Linienstrahler bzw. einen Kontinuumsstrahler. Für beide Fälle wird ein theoretischer und experimenteller Vergleich zwischen der Gestalt der Eichkurven, der Grösse des Signals und der Nachweisgrenze vorgenommen. Die Bedeutung der spektralen Bandbreite des Monochromators und des Absorptionslinienprofils wird diskutiert. Mit einem guten Monochromator mittlerer Dispersion bietet ein Kontinuumsstrahler bestimmte Vorteile und ergibt Nachweisgrenzen, welche annähernd gleich denen sind, die mit der Hohlkathodenlampe erhalten werden.

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HIGH-PRECISION ANALYSIS OF NUCLEAR MATERIALS BY CONSTANT-CURRENT COULOMETRY

PART I. DETERMINATION OF URANIUM

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As part of an analytical programme supporting work on basic nuclear data measurement, methods for the analysis of high-purity reference materials with precision and accuracy better than 0.01% have been required. This paper reports the application of constant-current coulometry to the problem of determining uranium; the determination of thorium will be described in a later paper.

Although not essential in the present standardisation work, methods applicable to nitric acid solutions were considered since analyses in this medium frequently arise in connection with nuclear fuel processing.

Many volumetric methods have been described for the precise determination of uranium[1-3] based on oxidimetric titration of uranium(IV). When high accuracy is sought, problems in the choice of suitable primary standards can arise, and coulometric methods based on the use of the Faraday as independent physical standard are advantageous. Controlled-potential coulometry in sulphuric acid electrolyte has proved reliable for the determination of uranium and is subject to relatively few interferences[4,5]. Precision, however, is limited to about 0.05% by the nature of background current corrections and difficulties inherent in precise current integration. A differential application of this technique has been recently applied in this laboratory[6] and shown to give a precision of 0.006%. This has proved useful for inter-comparison of uranium standards but is not an absolute technique.

The work of TAYLOR *et al.*[7-9] at the National Bureau of Standards, and recently of COOPER AND QUAYLE[10], has clearly demonstrated the advantages of constant-current coulometry for absolute standardisation, the precision and accuracy obtained for a wide range of chemical systems being equal to or in some cases, exceeding that of classical methods.

Several constant-current coulometric procedures have been described for the determination of uranium, the most direct involving titration of uranium(IV) with electrogenerated titanium(III)[11]. This has been applied to high-precision standardisation of uranium[12] but the method is inapplicable to nitric acid solutions and is somewhat time-consuming. An alternative procedure[13], involves reduction of U(VI) to U(IV), reaction with iron(III) and subsequent titration of iron(II) with electrogenerated cerium(IV). We have investigated further the potentialities of this procedure for high-precision work, using titanium(III) as reducing agent, excess being destroyed by oxidation with nitric acid containing sulphamate as described by CORPAL AND REYNAUD[14] and as applied to the precise assay of plutonium by COLEMAN AND HORNSBY[15]. Somewhat conflicting evidence is available for the suitability of electrogenerated cerium(IV) in high-precision coulometry because of the reported low current efficiency of this process. Distinction must clearly be made between actual current efficiency for generation of cerium(IV), shown to be well below 100%[16] and the overall titration efficiency in which direct electro-oxidation of the titrated species, in this case iron(II), predominates for the major part of the titration. The efficiencies of both these processes will be dependent upon current density and, in view of the wide range of experimental conditions described by various workers, this aspect of the problem was studied in some detail. In addition, the instability of uranium(IV) solutions to catalytic and air oxidation, and the choice and pretreatment of electrodes for electrogeneration were investigated.

EXPERIMENTAL

Apparatus

Cell assembly. The cell is of conventional design, consisting of a flat-bottomed 35-mm diameter pyrex glass beaker, 70 mm in height, fitted with a polythene cap, drilled to accommodate the anode compartment, electrodes and a glass tube for entry of nitrogen gas. The solution in the cell is stirred magnetically by means of a glass-covered stirring bar 20 mm in length. The anode compartment consists of a glass tube 8 cm in length and 1 cm in diameter, closed at one end by a porosity-4 glass sinter. Free flow of anolyte (saturated potassium sulphate in 0.5 *M* sulphuric acid) is prevented by a 2-cm agar plug containing potassium sulphate.

Electrodes. Reference—Pye wick-type saturated calomel electrode (S.C.E.).

Cathode—Platinum sheet 50 × 5 mm.

Anode—A cylinder of 48-mesh expanded gold sheet, 32 mm in diameter, 32 mm deep, supported on a 1-mm diameter gold wire. The total effective area was estimated to be 70 cm^2 for both sides.

Indicator—Platinum sheet with a total area of 0.5 cm^2.

Coulometer. The constant-current coulometer was designed and constructed in this establishment. The instrument provides 11 increments of current from 250 μA to 200 mA and is operated in conjunction with a Harwell-type 1350A timer as described by MONK AND STEED[17]. Provision is made for selection of an internal dummy resistance equal to that of the cell and through which current flows when the cell is out of circuit.

Time measurement is based on a 100 c/s signal provided by an external 10 kc/s quartz crystal oscillator with suitable solid-state frequency dividers. The crystal is not temperature-controlled but was shown to give an accuracy of better than 1 p.p.m. by comparison with standard broadcast frequencies.

Short-term current stabilisation (several hours) is better than 0.001% and the actual magnitude of the current is determined by measuring the voltage, developed across a Tinsley 4-terminal standard resistor (calibrated against NPL standards) in series with the cell, by means of a Cambridge Vernier potentiometer. It is estimated that the overall error in measuring the total number of coulombs consumed does not exceed 0.002%.

Weighing of samples

All weighings were made to ±0.02 mg using weights calibrated against NPL certified standards, appropriate corrections for air buoyancy being applied. Solutions were conveniently dispensed from weighed 7-ml polythene ampoules with finely drawn tips, electrostatic effects in the weighing of these ampoules being avoided by fitting a small gold gauze collar around the neck of the ampoule.

End-point detection

Titrations were performed potentiometrically using a platinum–S.C.E. electrode system, precise location of the end-point being established where the second derivative $\Delta^2E/\Delta t^2$ became zero. All calibrations were based on the 1961 ^{12}C atomic weight scale[18], the atomic weight of natural uranium being 238.03. The value of the Faraday used was 96,487 coulombs per g equivalent corrected to the ^{12}C scale.

Reagents

Cerium(III) sulphate–iron(III) sulphate electrolyte. Prepare 1 l of a saturated solution of cerium(III) sulphate octahydrate in 2 *M* sulphuric acid, allow to stand overnight and filter. Add a filtered solution of 8 g of iron(III) sulphate dissolved in the minimum of 0.5 *M* sulphuric acid. Before use, add a dilute solution of iron(II) or cerium(IV) sulphate until the potential of a platinum indicator electrode immersed in the solution is 790–810 mV with respect to S.C.E.

Titanium(III) sulphate solution (approx. 0.4 M). Dissolve 1 g of "Specpure" titanium sponge in 40 ml of 3.5 *M* sulphuric acid in a narrow-necked 50-ml flask containing a small funnel covered with a watch glass to minimise entry of air. Warm the flask to initiate the reaction and heat until dissolution is complete. Transfer the solution to a storage bottle (containing a small quantity of high-purity cadmium metal) fitted with a stopper with a nitrogen inlet tube and a inlet hole for a 1-ml pipette (both stoppered when not required). Bubble nitrogen through the solution for 15 min, to remove traces of reducing gases.

Analytical-reagent grade sulphuric acid was used throughout.

Investigation of the method

The method investigated involved the following operations: (1) reduction of uranium(VI) to uranium(IV) by addition of a slight excess of titanium(III) to a sulphuric–nitric acid solution containing sulphamate; (2) oxidation of excess of titanium(III) by nitric acid; (3) addition of excess iron(III) in a sulphuric acid solution saturated with cerium(III); and (4) titration of the equivalent iron(II) with electrogenerated cerium(IV).

Preliminary investigations showed that careful control of a number of factors was necessary to obtain high precision.

Choice and treatment of working electrode. A gold anode was found to be greatly superior to platinum for electrogeneration of cerium(IV), giving lower and more reproducible reagent blanks. This effect, presumably related to the formation of oxide films on the electrode surface, has been used to advantage in the controlled potential oxidation of plutonium(III)[19].

For best reproducibility chemical pretreatment of the electrode surface was necessary and the technique described by MARINENKO AND TAYLOR[9] involving oxidation with chromic acid followed by reduction with iron(II) was used. Both working and indicator electrodes were pretreated in this way and stored in chromic acid when not in use.

Preparation and storage of titanium(III) sulphate. Solutions of titanium(III) sulphate, if allowed access to air become oxidised and brown in colour. Careful preparation and storage under inert conditions is essential. Solutions stored over a small quantity of cadmium metal remain stable for several days.

Oxidation of uranium(IV). Low results were obtained if solutions, to which titanium(III) had been added, were allowed to stand in air before addition of iron(III)–cerium(III) reagent. These were probably due to oxidation of uranium(IV) by air, either directly, or catalytically in the presence of titanium(IV) or other metallic impurities. Certainly both processes have been reported, the latter particularly in the presence of copper(II), and this was confirmed by carrying out uranium determinations in the presence of this ion. Determinations in the absence of air, by blowing nitrogen over the surface of the solution after addition of titanium(III), showed that no significant oxidation occurred under these conditions, even in the presence of copper(II). The results are summarised in Table I using uranium of 99.972% purity.

TABLE I

EFFECTS OF AIR AND COPPER(II) ON OXIDATION OF U(IV)

Copper absent			*Copper present (solutions stood for 15 min)*		
Time of standing (min)	*Air present*	*Air absent*	*Cu (μg)*	*Air present*	*Air absent*
6	100.013	—			
8	99.973	—	5	99.75	—
10	99.987	—	20	99.35	99.979
12	99.950	99.979			
18	99.917	—			
30	—	99.982			

Current efficiency. The importance of current efficiency studies in constant-current coulometry has been discussed in detail by LINGANE[20] who emphasises the distinction between overall titration efficiency, involving direct electro-oxidation of the titrated species, and the actual current efficiency for electrogeneration of titrant. For the Ce(III)/Ce(IV) system, current efficiency has been shown to be less than 99.9%, yet many workers have obtained net titration efficiencies close to 100% for the titration of iron(II). The nature of the present work, in which high precision and accuracy was demanded, prompted some further investigation into current efficiency effects.

The *overall titration efficiency*, was determined over a range of current densities by analysis of solutions prepared from uranium of 99.972% purity (USAEC Dingot metal). Results showed that up to current densities of about 5 mA per cm^2, 100% efficiency is obtained; at higher values a small but significant reduction occurs, being 99.97% at 18 mA per cm^2. Since the proportion of direct electro-oxidation of iron(II) increases at lower current density it is desirable to use a large working electrode. In practice, with 50 mA for titration of 40 mg of uranium, the current density was 0.7 mA per cm^2.

The *current efficiency* for electrogeneration of cerium(IV) ions, as a function of current density, was determined by measuring current–voltage curves for the Ce(III)–Fe(III) electrolyte and for 2 *M* sulphuric acid alone using a gold anode of known area. Results are presented graphically in Fig. 1 and show that a maximum current efficiency of 99.9% is obtained above 3.34 mA per cm^2. It was also observed that above 6 mA per cm^2 the current efficiency falls below 99.90%. At the current density finally selected for the procedure (0.7 mA per cm^2) the current efficiency is 99.66%.

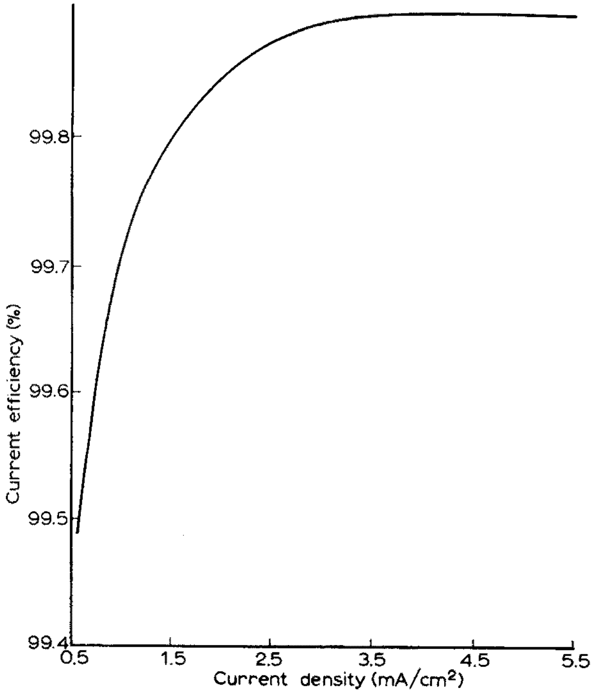

Fig. 1. Current efficiency for electrogeneration of cerium(IV) as a function of current density.

The extent of *direct electro-oxidation* of iron(II) at a current density of 0.7 mA per cm^2 was determined using a saturated cerium(III) sulphate solution in 2 *M* sulphuric acid which was $1.8 \cdot 10^{-2}$ *M* in iron(III) and $1.1 \cdot 10^{-1}$ *M* in iron(II), by following the anode potential during titration.

From the results shown graphically in Fig. 2a it is seen that direct electro-oxidation of iron(II) proceeds for about 80% of the titration, at which point the anode potential rises to a value at which simultaneous electrogeneration of cerium(IV) can occur. Further experiments carried out in the absence of cerium(III) in which current was passed for various fractions of the total titration time, followed by estimation of remaining iron(II) by potentiometric determination with standard dichromate solution, confirmed that 100% efficiency is maintained for about 80% of the titration (curve b in Fig. 2). Therefore, at a current density of 0.7 mA per cm^2 a current efficiency of only 99.66% for electrogeneration of cerium(IV) would be maintained for about 20% of the titration and this would lead to a positive bias of 0.06%. The fact that no bias is observed indicates that under conditions where the cerium(IV) concentration at the electrode surface is low, because of reaction with iron(II), a current efficiency of 100% is in fact achieved, although this is not the case in current–voltage experiments.

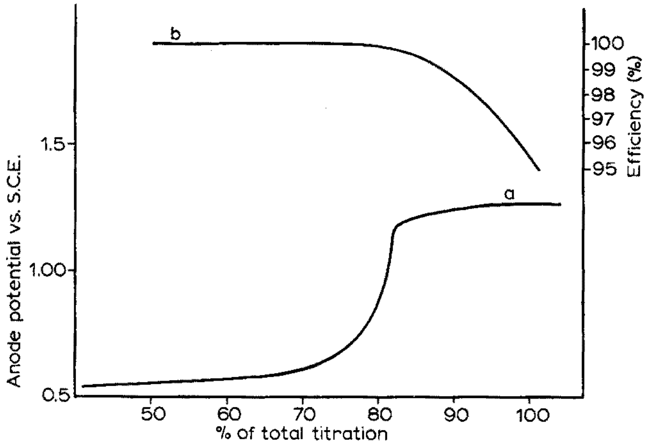

Fig. 2. Extent of electro-oxidation of iron(II).

Procedure

Preparation of metal samples. Clean the surface of the metal by immersion in hot 6 *M* nitric acid, followed by thorough washing with water and acetone. When dry, weigh about 2 g of sample to ±0.02 mg and transfer to a 50-ml conical flask fitted with a B19 air condenser. For low-purity metal, dissolution in 6 *M* nitric acid is satisfactory; but for higher-purity material this is very slow and the following method is used. Add 10 ml of 3 *M* hydrochloric acid to the sample and when dissolved add sufficient 6 *M* nitric acid to oxidise the uranium to the hexavalent state. Add 20 ml of 9 *M* sulphuric acid, evaporate the solution to fumes under an infrared lamp and finally fume on a hot plate for a few minutes. Transfer the solution to a weighed 100-ml measuring flask using a solution 2 *M* in sulphuric acid and 3 *M* in nitric acid, dilute to about 100 ml and re-weigh.

Preparation of oxide samples. NBS 950^{A} U_3O_8 is first heated at 900±20° for 1 h and then cooled in a desiccator. Dissolve about 2.4 g, weighed to ±0.02 mg, of oxide in 6 *M* nitric acid and prepare a solution as described above.

Coulometric titration. Transfer to the titration cell, containing the magnetic stirring bar, about 2 g of uranium solution dispensed from a 7-ml polythene ampoule and weighed to 0.02 mg. Add 0.5 g of sulphamic acid, start the magnetic stirrer and then introduce 1 ml of titanium(III) sulphate solution. Immediately cover the cell with a watch glass and introduce a steady stream of nitrogen via a narrow glass tube bent near one end to permit entry between the cover glass and the top of the cell. Gently swirl the contents of the cell and allow to stand with nitrogen flowing for 15 min. Add 25 ml of cerium(III)–iron(III) electrolyte from a pipette, washing down the cell walls with this reagent. Insert the pretreated, washed gold anode and attach the polythene cap containing the cathode, platinum and calomel electrodes and nitrogen inlet tube. Pass a current of 50 mA through the cell until the potential of the platinum indicator electrode (initially at 450 mV) reaches approximately 650 mV with respect to the S.C.E. Reset the timing unit to deliver 0.1-sec pulses of current and record the potential after each pulse, allowing 2 min to reach a steady value; continue to a potential of 950 mV.

Determine the current at intervals during the titration by measuring the voltage developed across a precision resistor using a Vernier potentiometer.

Carry out a reagent blank on 2 ml of 2 M sulphuric–3 M nitric acid in the absence of sample.

Calculate the titration time (t sec) as follows

$$t = t_B + \frac{A - B}{2A - (B + C)} D$$

where A = maximum change in potential per pulse of current, B = change in potential for increment preceding A, C = change in potential for increment following A, D = duration of current pulse in sec, and t_B = total titration time up to the end of increment B.

Correct for the reagent blank t_R: $t_c = t - t_R$

$$\% \text{ purity of uranium} = t_c i W/w \ 192.74$$

where t_c = corrected titration time in sec, i = current in A, W = atomic weight of uranium on ^{12}C scale, and w = weight of uranium sample (in g) corrected for air buoyancy.

RESULTS

Blank correction

Reagent blanks for different batches of cerium(III)–iron(III) electrolyte are often extremely high and variable owing to the presence of different amounts of cerium(IV) in the cerium(III) sulphate. Although it is not possible to pretitrate the oxidisable impurities electrolytically, before addition of uranium, satisfactory reagent blanks are obtained if the composition of the bulk electrolyte is adjusted, as described under reagents, to give a potential near to that of the equivalence point. By this method blanks of less than 0.5 sec, reproducible to within 0.01 sec are obtained and by careful preparation and storage of titanium(III) solution, as described earlier, this reproducibility is maintained for different preparations.

Analysis of uranium reference materials

Three reference materials were used to evaluate the procedure described.

(*1*) Dingot natural uranium metal supplied by the New Brunswick laboratory of the USAEC. This has been analysed by a number of US laboratories and it is believed that the assay value of 99.97% is accurate to within 0.01%. Recent work at the National Bureau of Standards[12] using constant-current coulometry has confirmed this, a value of 99.973 ± 0.004, for 95% confidence, being obtained.

(*2*) A low-purity natural uranium standard supply by the UKAEA Production Group laboratories, Springfields. This is used as a secondary standard, an assay of

$99.75 \pm 0.01\%$ being obtained by the method of Duckitt and Goode[21] which correlates well with 99.74% by difference from analysis of 33 impurity elements.

(3) National Bureau of Standards 950^A U_3O_8, certified at $99.94 \pm 0.02\%$ after ignition at 900°.

The precision and accuracy of the analytical method described was assessed by analysis of a number of solutions prepared from each material. Results are summarised in Table II.

TABLE II

ANALYSIS OF URANIUM STANDARDS

Sample	*Assay %*							
	Dingot metal				*UKAEA standard*		*NBS* 950^A U_3O_8	
	99.979	99.968	99.974	99.968	99.752	99.750	99.941	99.956
	99.983	99.968	99.972	99.967	99.748	99.747	99.943	99.955
	99.982		99.973	99.973	99.751		99.943	
			99.967	99.972	99.758			
			99.969	99.974	99.752			
			99.976	99.974	99.755			
				99.975	99.750			
				99.963	99.752			
				99.969	99.758			
					99.755			
Mean	99.981	99.968	99.972	99.971	99.753	99.748	99.942	99.955
Standard deviation of each set	0.002	—	0.003	0.004	0.003	0.002	0.001	0.001
Overall mean	99.972				99.752		99.948	
Standard deviation of all results	0.005				0.003		0.007	

DISCUSSION

Results in Table II show that a precision of 0.004% can be obtained at the 40-mg level and the accuracy appears to be better than 0.01% by comparison with alternative assay methods based on chemical standards. There is some indication from the results that the error involved in preparation of solutions is greater than that inherent in the procedure itself but this is not conclusive from the data presented. The method is not, of course, specific for uranium, any material capable of reduction with titanium(III) being titrated; however, for materials considered in this work only iron (< 30 p.p.m. for Dingot metal and U_3O_8 and 280 p.p.m. for the UKAEA standard) would lead to significant interference and appropriate corrections for this element were applied. The rather complex 4-compartment cell used by Taylor *et al.* does not appear essential for high accuracy and precision to be obtained and, with the simple system used here, no significant amount of material from the main cell compartment was detected in the anolyte.

The work described emphasises the problems which arise when analytical procedures are extended to their limit and shows clearly the importance of careful standardisation of conditions, and attention to detail which are necessary to obtain a very high order of precision and accuracy.

We thank Mr. K. H. HUGHES for helpful discussion on electrical standardisations and for calibration of equipment.

SUMMARY

Work is described on the application of constant-current coulometry for the highly precise and accurate assay of uranium and its compounds. Uranium is reduced to the tetravalent state by titanium(III) in nitric acid solution containing sulphamate and reacted with excess of iron(III) to give an equivalent amount of iron(II) which is titrated with electrogenerated cerium(IV). Factors governing the overall titration efficiency are discussed and results for the assay of a number of standard uranium materials presented. The procedure gives a standard deviation of 0.004% at the 40-mg level and an accuracy exceeding 0.01%.

RÉSUMÉ

On décrit un procédé pour le dosage de l'uranium et de ses composés par coulométrie à courant constant. L'uranium est réduit à l'état tétravalent par le titane(III) en solution nitrique, en présence de sulfamate; après réduction, il réagit avec le fer(III) pour donner une teneur équivalente en fer(II) qui est titré par le cérium(IV) formé électrochimiquement. Cette méthode donne une déviation standard de 0.004% pour 40 mg et une précision dépassant 0.01%.

ZUSAMMENFASSUNG

Mit der Konstant-Strom-Coulometrie werden sehr genaue und richtige Analysen des Urans und seiner Verbindungen durchgeführt. Das Uran wird durch Titan(III) in salpetersaurer Lösung zur vierwertigen Stufe reduziert. Es reagiert dann in der Lösung, die Sulfamat enthält, mit einem Überschuss von Eisen(III) und ergibt einen äquivalenten Betrag Eisen(II), der mit elektroerzeugtem Cer(IV) titriert wird. Faktoren, die die Gesamt-Titrationswirksamkeit bestimmen, werden diskutiert und Ergebnisse für die Analysen einer Anzahl von Uranmaterialien angegeben. Das Verfahren besitzt eine Standardabweichung von 0.004% beim 40-mg Bereich und eine Genauigkeit von weniger als 0.01%.

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DETERMINATION COULOMETRIQUE D'ALCALOIDES ET DE SELS DE BASES ORGANIQUES APRES PRECIPITATION SOUS FORME DE TETRAPHENYLBORATES

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(Reçu le 14 Octobre, 1966)

Lors d'un précédent travail[1], nous avons étudié avec succès la titration coulométrique de l'anion tétraphénylborate par l'argent(I) électrogénéré. Ce procédé nous a permis de doser avec succès des quantités de potassium, de césium et de rubidium comprises entre 0.3 et 10 mg. Le présent mémoire se propose d'étendre cette méthode à la détermination quantitative de sels d'alcaloïdes et d'autres bases organiques d'intérêt pharmaceutique et toxicologique. Les tétraphénylborates de ces bases étant, pour la plupart, très peu solubles dans l'eau, il est aisé de les isoler quantitativement.

Le dosage gravimétrique de ces composés a été réalisé primitivement par SCHULTZ ET MAYER[2] et par KELLER ET WEISS[3], mais ce procédé s'indique très peu pour les microdéterminations et de plus, comme nous avons pu le montrer précédemment[1], les tétraphénylborates sont assez instables à la dessiccation.

Deux méthodes particulièrement intéressantes du point de vue analytique sont à signaler dans la littérature. Celle de GAUTIER et de ses collaborateurs[4], qui préconisent une titration en milieu non aqueux, en se basant sur le fait que dans l'ion tétraphénylborate la base présente une polarité d'autant plus forte qu'elle se trouve dans des solvants acides et que la polarité acide qui lui est associée devient corrélativement négligeable. Cette méthode n'est pas applicable à l'échelle microanalytique, les auteurs précités travaillant sur des prises d'essais de bases azotées comprises entre 40 et 200 mg.

L'autre technique est celle proposée par FLASCHKA et ses collaborateurs[5,6] qui décrivent une méthode volumétrique basée sur la décomposition en milieu alcalin de l'anion tétraphénylborique par les sels de mercure, décomposition qui libère 3 protons titrables par les voies de l'acidimétrie usuelle: cette technique est particulièrement longue et n'est pas universelle, étant donné que certains composés basiques peuvent être partiellement détruits par le traitement alcalin. Par contre, la méthode coulométrique que nous proposons est rapide, extrêmement précise et applicable à l'échelle microanalytique.

Nous avons pu montrer[1] qu'il était possible de doser de petites quantités d'ion tétraphénylborate en nous basant sur la réaction chimique suivante:

$$(C_6H_5)_4B^- + Ag^+ \rightarrow (C_6H_5)_4BAg \downarrow$$

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l'ion argent étant produit électrolytiquement au sein même de la solution. Nous avons ainsi déterminé des quantités de cet ion allant jusqu'à 1 mg avec une erreur moyenne n'excédant pas ±0.4%.

Ces résultats nous ont incités à étudier et à appliquer la méthode coulométrique à la détermination de certains sels de bases organiques.

PARTIE EXPÉRIMENTALE

Réactifs

Les sels de bases organiques et les sels d'alcaloïdes utilisés sont soit de qualité "Pharmacopée Belge P.B.V.", soit de provenance K and K Laboratories (Plainview, N.Y.). Des solutions aqueuses mères des sels étudiés ont été préparées fraîchement chaque jour. Généralement celles-ci titraient 100 mg/l et dans certains cas bien précis, 500 mg/l. La papavérine base, pour sa part, a été dissoute à l'aide d'acide acétique à 1 %.

La solution précipitante de tétraphénylborate est à 1% dans la soude 0.02 *M*. L'adoption du milieu alcalin est réalisée en vue d'éviter une décomposition trop rapide du réactif précipitant. L'utilisation de cette solution n'excède en tout cas pas une semaine.

La solution d'électrolyte de support est constituée par une solution 0.4 *M* de nitrate sodique (A. R., Mallinckrodt) dans l'acétone (purissimum) à 30% v/v.

Appareillage

La cellule coulométrique d'une capacité de 125 ml comprenant une anode génératrice d'ions argent et une cathode auxiliaire en platine, est essentiellement identique à celle décrite par LINGANE[7] pour la titration coulométrique des halogènes. Le cours de l'opération est suivi potentiométriquement à l'aide du système d'électrodes: argent–calomel.

Le circuit coulométrique est identique à celui décrit précédemment[1].

Procédé général

Une partie aliquote de la solution mère du sel de bases organiques est traitée par 0.2 ml d'acide acétique et 1 ml de la solution d'acétate sodique 2 *M* (A.R., Mallinckrodt) de façon à amener le pH dans une zone voisine de 4.5. On y ajoute 5 gouttes de la solution aqueuse à 5% de chlorure d'aluminium et le liquide est porté à une température de 40 à 50° au bain marie. Le réactif précipitant est ajouté goutte à goutte, en agitant énergiquement, et le tout est maintenu à 40°–50° pendant 1h. Après refroidissement, la filtration s'effectue sur entonnoir d'Allinh (G4) en s'aidant d'un vide léger. Le vase à précipitation est lavé à l'aide de 3 fois 2 ml de la solution d'acide acétique à 1%. Le précipité est alors soigneusement dissous dans l'acétone et la solution acétonique obtenue est transférée quantitativement dans la cellule coulométrique. L'électrolyte de support est alors ajouté et la titration coulométrique est effectuée comme décrite précédemment[1].

RÉSULTATS ET DISCUSSION

L'acide tétraphénylborique forme des sels normaux (1 équivalent basique

TABLEAU I

DÉTERMINATIONS COULOMÉTRIQUES D'ALCALOÏDES ET DE SELS DE BASES AZOTÉES

	Prise d'essai (mg)	*Nombre d'essais*	*Trouvé (mg)*	*Différence (mg)*	*Erreur (%)*
Papavérine base	10	2	10.01 ± 2	+0.01	+0.1
$C_{20}H_{21}NO_4$	5	2	4.988 ± 5	−0.012	−0.24
	2	2	1.992 ± 2	−0.008	−0.4
Atropine SO_4	20	1	19.92	−0.08	−0.4
$(C_{17}H_{23}NO_3)_2H_2SO_4 \cdot H_2O$	10	3	9.860 ± 3	−0.14	−1.4
Pilocarpine NO_3	10	2	9.913 ± 7	−0.087	−0.87
$C_{11}H_{16}N_2O_2 \cdot HNO_3$	5	2	4.97 ± 2	−0.030	−0.6
	2.5	1	2.48	−0.02	−0.9
Thiamine chl.	10	3	9.975 ± 5	−0.025	−0.25
$C_{12}H_{17}ClN_4OS \cdot HCl \cdot H_2O$	5	2	4.990 ± 4	−0.010	−0.20
Spartéine SO_4	10	1	10.6	+0.6	+6
$C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$	20	1	18.5	−1.5	−7.5
Yohimbine chl.	10	3	9.955 ± 65	−0.045	−0.45
$C_{21}H_{26}O_3N_2 \cdot HCl$	5	2	4.975 ± 25	−0.025	−0.5
Procaïne chl.	10	3	10 ± 9	—	—
$C_{13}H_{20}N_2O_2 \cdot HCl$	6	2	5.94 ± 3	−0.060	−0.9
	3	1	2.955	−0.045	−1.5
Strychnine SO_4	10	3	9.980 ± 9	−0.020	−0.2
$(C_{21}H_{22}O_2N_2)_2 \cdot SO_4H_2 \cdot 5H_2O$	5	3	5.003 ± 5	+0.003	+0.06
Tetracaïne chl.	10	2	9.815 ± 15	−0.185	−1.85
$C_{15}H_{24}N_2O_2 \cdot HCl$	20	1	19.80	−0.2	−1
Eserine SO_4	10	3	9.81 ± 10	−0.19	−1.9
$(C_{15}H_{21}N_3O_2)_2 \cdot H_2SO_4$					
Quinine base	10	2	9.74 ± 5	−0.26	−2.6
$C_{20}H_{24}N_2O_2$	5	1	4.900	−0.100	−2
	2	1	1.966	−0.034	−1.7
Brucine SO_4	10	3	9.900 ± 6	−0.100	−1
$(C_{23}H_{26}N_2O_4)_2 \cdot H_2SO_4 \cdot 7H_2O$	5	2	4.942 ± 4	−0.058	−1.15

+1 équivalent acide) avec les bases étudiées au cours de ce travail. Seule la quinine (Q) fournit le sel neutre: $[(C_6H_5)_4BH]_2Q$.

Le Tableau I mentionne les résultats obtenus avec des bases organiques, des alcaloïdes de structures diverses, et quelques anesthésiques locaux. Nous pouvons constater que les résultats obtenus sont très satisfaisants dans le plupart des cas. Seul le cas du sulfate de spartéine peut paraître aberrant. En effet, le composé formé entre l'ion tétraphénylborique et la spartéine est, à l'inverse des autres, relativement insoluble dans l'acétone et lors de l'addition de la solution d'électrolyte de support en vue du dosage coulométrique, on observe rapidement une reprécipitation du tétraphénylborate de spartéine qui freine considérablement l'établissement du potentiel au moment du point final. De ce fait, l'opération est très longue et le degré d'incertitude devient très grand quant à l'établissement du point d'équivalence de la réaction. Plusieurs déterminations effectuées sur 10 mg de sulfate de spartéine nous ont donné des résultats compris entre 92 et 106%. Un moyen de résoudre ce problème coulométriquement serait de générer un excès d'ions argent, de le laisser réagir jusqu'à fin de la réaction et de déterminer l'excès d'argent restant en solution.

En ce qui concerne la précipitation des tétraphénylborates de pilocarpine et d'anesthésiques locaux, nous avons pu constater qu'étant donné leur produit de solubilité assez grand, la précipitation n'était parfaite que si l'on effectuait celle-ci sur des volumes relativement restreints de solution (de 3 à 5 ml).

Dans le cas du phosphate de choline, produit bien connu pour sa réactivité comparable à celle des alcaloïdes, nous n'avons pu éliminer la tendance que présente ce corps à former des précipités colloïdaux avec l'ion tétraphénylborique. L'addition d'une quantité complémentaire de la solution de chlorure aluminique qui a pour effet de favoriser la coagulation et de briser l'état colloïdal est restée inopérante dans ce cas.

Influence du pH

Contrairement aux cations étudiés antérieurement[1], la zone de pH optimale est plus restreinte ici et semble se situer entre 4.4 et 4.8. En effet, nous avons pu remarquer qu'à des pH voisins de 4, des corps tels que l'atropine par exemple ne précipitaient qu'à concurrence de ±85% et qu'il en est de même si l'on opère à des pH supérieurs à 5.

Effet de la température

Alors que dans le cas du potassium, une température de 70° permet une excellente coagulation du précipité, cette température a un effet désastreux sur certains tétraphénylborates d'alcoloïdes et notamment sur celui de la quinine qui est largement hydrolysé à cette température. Une température comprise entre 40° et 50° est considérée comme optimale dans les cas étudiés au cours de ce travail.

Effet de la vitesse de filtration

Nous devons également insister sur un fait technique qui peut se révéler important: la succion par le vide lors de la filtration doit se faire lentement car des précipités très ténus comme le tétraphénylborate d'yohimbine, par exemple, peuvent traverser aisément les pores d'un filtre de porosité même fine s'il est aspiré avec un vide trop poussé.

CONCLUSIONS

En conclusions, nous pouvons avancer que la méthode coulométrique proposée présente de nombreux avantages tels que: rapidité d'exécution (pas de gravimétrie ni d'extraction), précision très satisfaisante, et surtout, possibilité de travailler à l'échelle microanalytique. De plus, elle peut se combiner avec une méthode d'identification par point de fusion et examen microcristallographique des précipités de tétraphénylborates comme l'ont préconisés FISCHER ET KARAWIA[8].

Nous tenons à remercier la Belgian American Educational Foundation pour l'aide qu'elle a apportée à l'un de nous (G.J.P.).

RÉSUMÉ

Une microméthode coulométrique de détermination de sels de bases organiques et d'alcaloïdes est décrite. Ceux-ci sont préalablement précipités par le tétraphénylborate de sodium et le tétraphénylborate combiné est déterminé coulométriquement à l'aide de l'ion argent électrogénéré. Onze composés sont dosés avec une précision très satisfaisante.

SUMMARY

A coulometric microdetermination of salts of certain organic bases and alkaloids is described, based on precipitation as the tetraphenylborates and the coulometric determination of the tetraphenylborate content of the precipitate with electrogenerated silver ion. Eleven compounds were determined with satisfactory accuracy.

ZUSAMMENFASSUNG

Eine coulometrische Mikrobestimmung von Salzen bestimmter organischer Basen und Alkaloide wird beschrieben. Sie beruht auf der Fällung dieser Stoffe als Tetraphenylborat und der coulometrischen Bestimmung des Tetraphenylboratgehalts im Niederschlag mit electroerzeugten Silberionen. 11 Verbindungen wurden mit befriedigender Genauigkeit bestimmt.

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FLUORIMETRIC DETERMINATION OF LITHIUM WITH DIBENZOTHIAZOLYLMETHANE*

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Dibenzothiazolylmethane, $(C_7H_4NS)_2CH_2$, produces a specific fluorescence with zinc in ethanol–water solutions; it has been used for the detection and determination of zinc[1]. Lithium was reported to react also, when dioxane was used as a solvent, to give a brilliant blue fluorescence. The use of dibenzothiazolylmethane (DBM) as a reagent for lithium is reported in this paper.

EXPERIMENTAL

Apparatus

A 230-W mercury ultraviolet lamp, Hanovia type 16106, was employed for qualitative work. Quantitative measurements were made with a Turner Model III Fluorimeter and Rustrak recorder. The general purpose filters supplied with the fluorimeter were used (primary filter, 365 nm, Corning #7-60; the secondary filter passes wavelengths longer than 415 nm, color specification #2A). The quantity of incident ultraviolet light was controlled by the 4 adjustable slits (×1, ×3, ×10, ×30); for decreased sensitivity a secondary filter (color specification ND1%, Kodak #96), which reduced the normal incident light to 1 %, was used.

Solutions

The preparation and properties of DBM have been described previously[1]. Reagent solutions were prepared by dissolving DBM in spectro-quality dioxane; the concentration range of lithium predetermines the reagent concentration.

Reagent-grade potassium hydroxide was dissolved in freshly boiled doubly distilled water to give an approximately 2 *N* solution.

Spectrographically standardized lithium carbonate (0.53240 g) was dissolved in a litre of doubly distilled water to give a 100-p.p.m. lithium stock solution.

Determination of lithium

Lithium can be determined, by changing the fluorimeter range setting, in 4 concentration ranges, namely 0–0.8 μg, 0–3 μg, 0–6 μg and 0–20 μg.

Procedure

Transfer a 2.0-ml aliquot of a neutral aqueous solution containing 0.05–20 μg

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* This paper is abstracted from the M.Sc. thesis of A. E. PITTS.

of lithium to a 10-ml volumetric flask. Add 10 μl (syringe) of 2 *N* potassium hydroxide. Add 3 ml of a 0.002% DBM solution for 0–4 μg of lithium; a 5–10-fold excess is desirable for 4–20 μg. Dilute to 10 ml with dioxane. Measure the fluorescence against a similarly prepared blank.

Linear calibration graphs passing through the origin are obtained in three concentration ranges (0–0.2 μg Li, 0–1.6 μg Li and 0–4.0 μg Li) with sensitivity ranges of 10, 3 and 1 respectively. A reasonable working curve can be obtained for up to 20 μg (Fig. 1) using the sensitivity range × 10 with a 1% filter; for larger amounts of lithium, however, dilution is necessary.

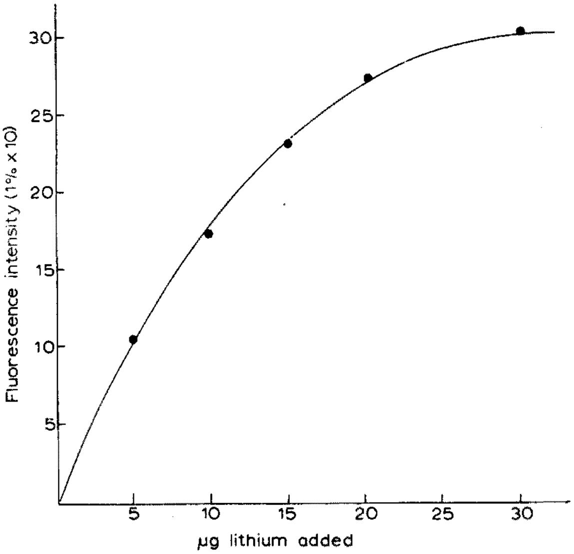

Fig. 1. Determination of lithium (sensitivity range × 10 with 1% filter).

Measurement of blank and sample fluorescence should be made at the same time interval after reagent addition. Although the fluorescence intensity of both blanks and samples are constant with time at low concentrations, there is fluorescence quenching at high lithium concentrations and, for accurate results, readings for both blank and sample should be made within 15 min and after the same time interval. The relative standard deviation of 5 measurements (mean fluorescence, 44) was 1.9%.

DISCUSSION

Factors affecting the determination

Since solvent structure can have a marked effect on the fluorescence efficiency, the lithium–DBM reaction was investigated in a number of spectro-quality solvents. There was no appreciable fluorescence in acetonitrile, dimethylformamide, ethanol, methanol, or pyridine; dioxane was the only solvent, of those examined, in which DBM reacted with lithium to fluoresce. The intensity of this fluorescence is greatly reduced if water is added; Fig. 2 shows the decrease in sensitivity as the amount of water is increased. However, there is a marked increase in fluorescence stability with increasing water concentration and, for analytical purposes, solutions containing 2 ml of water per 10-ml final volume give satisfactory intensity and reasonable stability.

Figure 3 shows the effect of potassium hydroxide concentration; for 4 µg of lithium the fluorescence rises sharply to a maximum of 60 with 0.02 mmoles of potassium hydroxide and is then constant. There is increased instability of blanks and samples when potassium hydroxide is in excess of 0.02 mmole and this amount, per 10-ml final volume, is recommended.

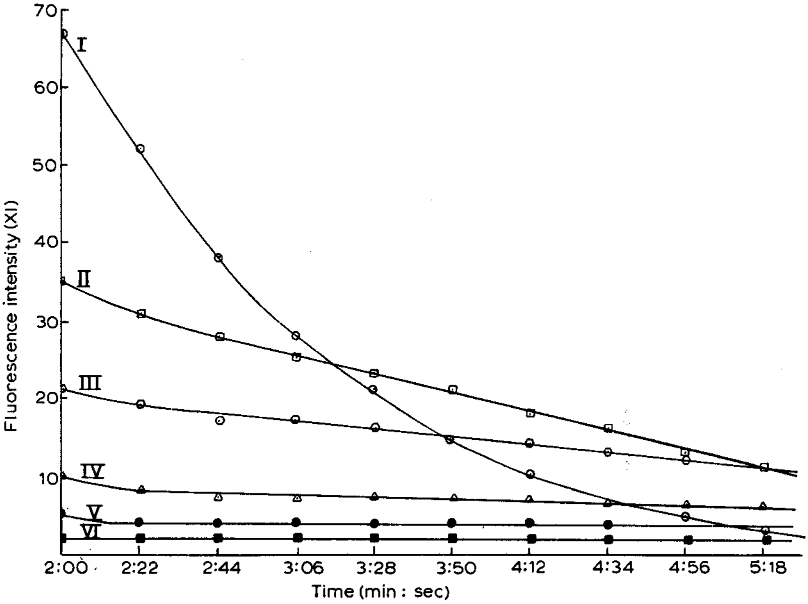

Fig. 2. The effect of fluorescence quenching due to addition of water (0.20 µg lithium in 10-ml samples). (I) 0.50 ml water, (II) 1.00 ml water, (III) 1.25 ml water, (IV) 1.50 ml water, (V) 1.75 ml water, (VI) 2.00 ml water.

Reagent solutions should be freshly prepared for highest sensitivity although satisfactory results were obtained with 2-day old reagent. With the × 1 slit, secondary filter and 1 µg of lithium, the readings varied from 40 with fresh reagent solution to 33 with 2-day old reagent.

Qualitative investigation of the reaction of DBM with metals in 55% dioxane–water solutions showed strong fluorescence for Li^+ and Zn^{2+} only. The following metal ions did not fluoresce: Na^+, K^+, Rb^+, Ag^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, B^{3+}, Al^{3+}, As^{3+}, Sb^{3+}, Bi^{3+}, Cr^{3+}, Fe^{3+}, La^{3+}, Zr^{4+}, Th^{4+}, Sn^{4+}, Ta^{5+}, Nb^{5+}, W^{6+}. Metals forming insoluble hydroxides are an interference but they may be easily removed before the determination of lithium by precipitation or ion-exchange methods[2].

The fluorescence of lithium with DBM is depressed when large amounts of anions are present. For example, the fluorescence intensity obtained for 1 µg of lithium using the standard procedure (1% filter, × 10 slit) was 17 with no sodium perchlorate present, 12 with 10 mg of sodium perchlorate in the 10 ml of final solution, and was constant at 5 when 40–80 mg of sodium perchlorate were added. Similar results were obtained in the presence of large amounts of nitrate and chloride ions. Although there is decreased sensitivity, the fluorescence is constant within certain concentration limits of each anion; Fig. 4 shows the excellent results obtained. More than 3 mg of sulphate should be excluded because of precipitation of metal sulphate in the dioxane–water solutions.

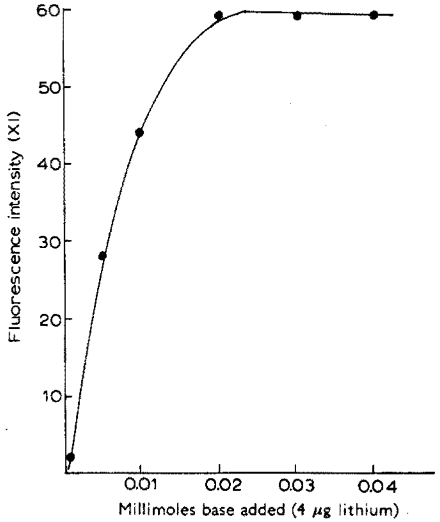

Fig. 3. Effect of potassium hydroxide concentration.

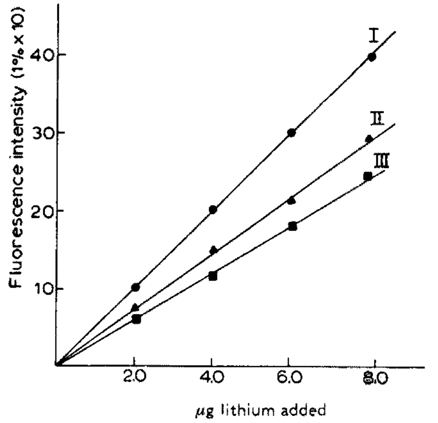

Fig. 4. Lithium determinations in the presence of 40 mg of (I) perchlorate ions; (II) nitrate ions; (III) chloride ions.

APPLICATIONS

Although 0.01 μg of lithium can be determined in pure solutions, the practical limit for the determination of lithium in salts is 0.5 μg. Lithium was determined in reagent-grade sodium, rubidium and strontium chlorides without difficulty. The regular procedure was followed but 40–80 mg of sample were taken for analysis and the blank contained the same amount of lithium-free potassium chloride. The percentage of lithium found in primary-standard sodium chloride (Thorn Smith) and strontium chloride hexahydrate (BDH) was 0.0035%; 0.035% lithium was found in a sample of rubidium chloride (Eimer and Amend). Lithium added to each of these salt solutions, as a check on the method, was accurately determined in each case.

Mixed anion alkali-metal salts were also analyzed by converting to perchlorates with perchloric acid. The procedure of SMITH AND ROSS[3] was used; samples were weighed into pyrex beakers and dissolved in a minimum amount of water, perchloric acid was added, and the solution was evaporated to dryness. After redissolving the residues in hot water, the samples were again evaporated to dryness; the converted perchlorate samples were dissolved in water, transferred to a volumetric flask and diluted to the mark. Aliquots (2 ml) containing 40–100 mg of perchlorate salt were taken for analysis and the regular procedure followed; the blanks contained 40–100 mg of perchlorate. Lithium added to alkali-metal salts, which were then treated by the above procedure, was determined without difficulty. The FLETCHER volatilization procedure[4] or the KALLMANN method[5] provides a means of isolating the alkali chlorides from mineral material containing lithium and, for trace amounts, the lithium could be determined fluorimetrically with DBM.

This work was suppoıted, in part, by the Defence Research Board of Canada.

SUMMARY

Lithium is determined by measuring the fluorescence produced on reaction with dibenzothiazolylmethane; zinc is the only other metal that fluoresces. The practical limits for the determination of lithium in salts are from 0.5 to 20 μg although 0.01 μg can be determined in pure solutions.

RÉSUMÉ

Le lithium est dosé par mesure de fluorescence produite par la réaction au dibenzothiazolylméthane. Seul le zinc donne une fluorescence. Les limites pratiques de dosage du lithium dans des sels varient de 0.5 à 20 μg; cependant il est possible de doser 0.01 μg dans des solutions pures.

ZUSAMMENFASSUNG

Es wird eine fluorimetrische Bestimmung von Lithium mit Dibenzothiazolylmethan beschrieben. Zink ist das einzige Metall, welches ebenfalls fluoresziert. Die praktischen Grenzen für die Bestimmung des Lithiums in Salzen liegen zwischen 0.5 und 20 μg, obwohl noch 0.01 μg in reinen Lösungen bestimmt werden können.

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THE APPLICATION OF RESONANCE MONOCHROMATORS TO THE DETERMINATION OF LITHIUM IN BLOOD SERUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Lithium therapy is used in the treatment of patients suffering from mania and consequently the lithium content of their blood needs to be determined to ensure that it does not exceed the toxic limit. Generally it is maintained at a concentration of approximately 1 meq/l, *i.e.* 7 μg/ml, in the serum.

Flame photometry has been applied to the determination of lithium in blood and blood serum by many workers including BARROW[1], LANG AND HERRMANN[2], NEVIUS AND LANCHANTIN[3] and MOGENS SCHOU[4]. Lithium in blood has been determined colorimetrically by PLUM[5]; this method is only semi-quantitative as is also a spectrographic technique described by SANTOS RUIZ *et al.*[6] for determining lithium in biological materials. SILVESTRI[7] and NEGINA *et al.*[8] have determined lithium in blood by emission spectrography.

Atomic absorption would appear to be an ideal technique for this determination as it has already been successfully applied to the determination of other metals in blood serum[9-11].

Apart from the work of ZAIDEL AND KORENNOI[12,13] on the determination of the isotopic composition of lithium and the work of PATASSY[14] on lithium determination in waters and plants, very little has been reported on the determination of lithium by the atomic absorption method proposed by WALSH[15].

The present work was undertaken in order to extend the application of the new technique described by SULLIVAN AND WALSH[16] in which the conventional dispersion-type monochromator generally used in atomic absorption spectrophotometry is replaced by a relatively simple "resonance monochromator". These authors have reported on the determination of calcium, magnesium, sodium and potassium in blood serum by this technique.

EXPERIMENTAL

Apparatus

Conventional atomic absorption spectrophotometer. The instrument used was a Techtron AA-2 spectrophotometer, similar to that described by BOX AND WALSH[17], incorporating a Zeiss M4QII silica prism monochromator set to isolate the lithium resonance doublet at 6708 Å with a spectral band pass of 30 Å. A selected I.P. 28

photomultiplier detected the signal from an argon-filled lithium hollow-cathode lamp operated at 8 mA on 100 c/sec.

An air/coal gas flame was found to be the most suitable for measuring lithium absorption. The spray chamber and the atomizer were of the "E.E.L." type (manufactured by Evans Electroselenium Ltd., England), the atomizer operating with an air consumption of 13 l/min and a sample consumption of 2 ml/min. With this atomizer a flow rate of approx. 2.3 l/min of coal gas provided the optimum flame conditions for lithium absorption. Maximum absorption was obtained by lowering the 10-cm tubular burner (0.05-cm slot) a few mm below the light path.

Resonance monochromator. The resonance detector providing lithium atoms by evaporation from lithium metal was similar in construction to that described by SULLIVAN AND WALSH[16]. It was operated at 5 A and 2 V D.C. The lamp source was a lithium hollow-cathode lamp operating on 10 mA (modulated). An RG 2 filter was placed between the resonance lamp and a R 136 photomultiplier.

To obtain the requisite signal with a resonance monochromator it is necessary to use a wider flame[16], thus permitting an increase in angular aperture of the optical system. A wider flame was produced with a flat-top, stainless steel burner with two 0.038-cm parallel slots, 0.5 cm apart and 7.5 cm long. The same atomizer and spray chamber as described previously were used with similar flame conditions.

Materials

Samples of blood serum were supplied by the Royal Park Psychiatric Hospital, Melbourne.

A standard solution containing 100 μg Li/ml was prepared by dissolving A.R. lithium sulphate in deionized water.

Development of method

Normal blood serum contains approximately 3500 μg Na/ml, 150 μg K/ml, 100 μg Ca/ml and 20 μg Mg/ml; therefore the effects of these metals in the appropriate concentrations on lithium absorption were investigated. Calcium and magnesium in the concentrations normally found in blood serum had no effect but sodium and potassium caused a very slight enhancement of the lithium absorption, about 3% in the presence of 350 μg Na/ml and 15 μg K/ml. Consequently calibrating solutions of lithium were made up to contain approximately the concentration of sodium and potassium present in the solutions of blood serum. These metals were added in the form of their chlorides dissolved in deionized water.

The blood serum by itself is too viscous and contained too high a salt concentration to be sprayed into the flame without causing rapid blockage of the burner slot because of deposition of salts inside the burner, so 1:5 dilutions of blood serum to water were first measured for lithium absorption and compared with calibrating solutions containing 700 μg Na/ml and 30 μg K/ml. The results were satisfactory but after repeated spraying the burner became partially clogged and had to be cleaned frequently so that for routine determinations, 1:10 dilutions of serum are recommended even though a factor of 2 in sensitivity is sacrificed.

Recommended procedure

Serum (0.5 ml) is diluted to 5 ml with deionized water.

Five calibrating solutions to cover the range 0–4 μg Li/ml are prepared by diluting the standard solution of 100 μg Li/ml with deionized water and incorporating 350 μg Na/ml and 15 μg K/ml in each.

With the experimental conditions previously described, the transmissions of the calibrating solutions and then the serum solutions are measured. This is repeated twice more and the results averaged. The average transmission values are then converted to absorbance and plotted against concentration. The lithium contents of the serum solutions are read from this graph and thence the lithium concentration in the original sera calculated.

RESULTS AND DISCUSSION

The results obtained for 1:10 dilutions of 6 samples of blood serum are given in Table I. The same solutions were used with both the conventional monochromator and the resonance monochromator.

TABLE I

LITHIUM IN BLOOD SERUM

Serum number	*Lithium concentration (μg/ml) in blood serum by atomic absorption spectrophotometry*				
	Techtron AA-2 instrument			*Resonance monochromator*	
	Diluted 1:20	*Diluted 1:10*	*Diluted 1:5*	*Diluted 1:10*	*Diluted 1:5*
1	3.6	3.6	3.75	3.6	3.65
2	2.2	2.05	—	1.9	—
3	2.6	2.4	2.6	2.2	2.5
4	2.6	2.4	2.6	2.2	—
5	—	4.8	4.8	4.4	4.7
6	—	3.6	3.4	3.3	3.45

The calibration curves obtained for each of the instruments for lithium in solutions containing 350 μg Na/ml and 15 μg K/ml are shown in Fig. 1. For comparison, the calibration curve obtained with the double-slot, 7.5-cm burner in conjunction with the conventional instrument is also shown. The shorter path-length of the double-slot burner is responsible for the difference in sensitivity between curves 1 and 2. Curve 3 is less sensitive than curve 2 because the angular aperture of the resonance system is wider and the flame is not used as effectively as in the conventional instrument. The signal:noise ratio was not high enough to allow the angular aperture of the resonance system to be reduced by a lens stop.

To show that there were no interference effects from other materials present in the samples, 1:5 and 1:20 dilutions of blood serum in water were measured relative to calibrating solutions containing the appropriate concentrations of sodium and potassium. These results are also included in Table I. The calibration curves for the lithium solutions containing 700 μg Na/ml, 30 μg K/ml and 175 μg Na/ml, 7.5 μg K/ml did not differ by more than 2% in sensitivity from the curves shown in Fig. 1. The slight enhancement of lithium absorption caused by the presence of sodium and potassium in the solutions actually decreased as the concentrations of sodium and potassium increased.

Lithium determinations on different aliquots of the same sample of serum, measured at different times, were reproducible to within ±0.2 μg/ml Li in the original serum.

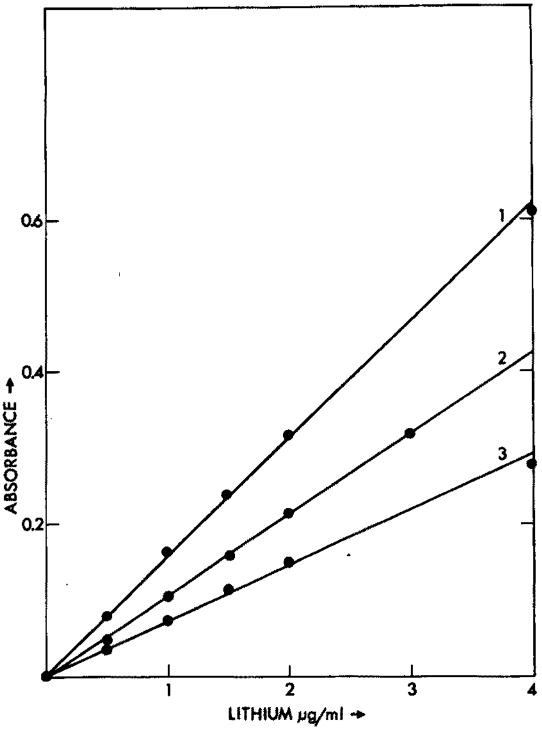

Fig. 1. Calibration curves for lithium in blood serum diluted 1:10 with water. Solutions contain 350 μg Na/ml and 15 μg K/ml. Curve 1: Conventional atomic absorption spectrophotometer with 10-cm burner. Curve 2: Conventional atomic absorption spectrophotometer with 7.5-cm double-slot burner. Curve 3: Resonance monochromator with 7.5-cm double-slot burner.

TABLE II

LITHIUM IN BLOOD SERUM BY THE STANDARD ADDITION METHOD

Serum number	*Li (μg/ml) in serum as determined by std. addition method (0.5 μg Li/ml added)*	
	Techtron AA-2 instrument	*Resonance monochromator*
1	4.0	3.6
2	2.3	1.9
3	2.6	2.2
4	2.7	2.4
5	4.6	4.4
6	3.5	3.6

Since the calibration curves for lithium are linear over the range studied, isolated determinations of lithium in blood serum may be rapidly carried out by the standard addition method which eliminates the need for constructing a calibration curve, *i.e.* if A_1 is the absorbance of the serum solution alone, A_2 the absorbance of the serum solution with a known amount of lithium added, and x the unknown lithium content of the serum solution, then $x/(x + \text{added Li}) = A_1/A_2$. Table II shows the results of standard addition measurements on the same 6 samples of blood serum used previously, diluted 1:10. These results agree within the experimental limits of reproducibility with those of Table I.

Table III gives the results of recovery tests in which known concentrations of lithium were added to the serum solutions before measuring their absorption. These results further indicate that there are no interference effects from other materials present in the solutions of blood serum.

TABLE III

RECOVERY EXPERIMENTS

Instrument used	*Dilution of serum*	*Li in solution (μg/ml)*	*Li added (μg/ml)*	*Li total (μg/ml)*	*Li recovered (μg/ml)*	*% recovery*
Techtron AA-2	1:10	0.23	0.5	0.73	0.73	100
Techtron AA-2	1:10	0.26	0.5	0.76	0.78	103
Techtron AA-2	1:10	0.38	0.5	0.88	0.87	99
Techtron AA-2	1:10	0.26	1.0	1.26	1.24	98
Techtron AA-2	1:10	0.38	1.0	1.38	1.40	101
Techtron AA-2	1:10	0.38	1.5	1.88	1.88	100
Techtron AA-2	1:5	0.68	1.0	1.68	1.66	99
Techtron AA-2	1:5	0.96	1.0	1.96	1.94	99
Resonance monochromator	1:10	0.21	0.5	0.71	0.70	99
Resonance monochromator	1:10	0.36	0.5	0.86	0.88	102
Resonance monochromator	1:10	0.44	0.5	0.94	0.94	100
Resonance monochromator	1:10	0.21	1.0	1.21	1.19	98
Resonance monochromator	1:10	0.36	1.0	1.36	1.36	100
Resonance monochromator	1:10	0.36	1.5	1.86	1.80	97
Resonance monochromator	1:5	0.69	1.0	1.69	1.74	103
Resonance monochromator	1:5	0.98	1.0	1.98	1.96	99
						Av. 99.8

With the power supply and amplifier used, some lithium emission from the flame was detectable when the solutions were sprayed. This emission varied between 0 and 3% of full-scale deflection depending on the concentration of lithium. However, at the absorptions measured, this low level of emission did not result in any error in the observed transmission reading. No emission from lithium in the flame is detectable if the amplifier is sharply tuned to the modulation frequency of the lamp power supply.

When the Techtron AA-2 instrument was used, it was observed that a $\frac{1}{8}''$-diameter aperture on the lens nearest the hollow-cathode lamp source increased the sensitivity of lithium absorption by a few percent. As mentioned previously such an aperture could not be used with the resonance monochromator because the resonance signal was not sufficiently intense. A high-intensity lithium hollow-cathode lamp source[18] would result in a resonance signal sufficiently intense to allow a reduction in aperture of the optical system and thus eliminate the necessity for a wider flame.

The author is indebted to Mr. J. V. SULLIVAN for suggesting this work and for helpful discussions, to Mr. W. G. JONES for constructing the resonance monochromator, and to Miss S. ANDREWS for supplying the samples of blood serum.

SUMMARY

Lithium in blood serum can be determined rapidly and with sufficient accuracy by atomic absorption measurement of solutions of blood serum diluted with water, using either a conventional atomic absorption spectrophotometer or one with a resonance monochromator. Calibrating solutions contain sodium and potassium at approximately the concentrations present in the serum solutions as these metals cause a slight enhancement of lithium absorption in the air/coal gas flame. Results are reproducible to within ±0.2 µg Li/ml in the serum and the limits of sensitivity attainable for samples diluted 1:10 are 0.3 µg Li/ml in the serum with the conventional instrument and 0.6 µg Li/ml in the serum with the resonance monochromator.

RÉSUMÉ

Le lithium dans le sérum sanguin peut être dosé rapidement et avec une précision suffisante par spectrophotométrie par absorption atomique. On utilise soit un spectrophotomètre par absorption atomique conventionnel soit un appareil avec monochromateur à résonance. Limite de sensibilité (pour des échantillons dilués 1:10): 0.3 µg/ml Li dans le sérum avec l'appareil conventionnel et 0.6 µg/ml Li avec le monochromateur à résonance.

ZUSAMMENFASSUNG

Lithium kann im Blutserum mittels der Flammenabsorptionsspektroskopie schnell und mit genügender Genauigkeit bestimmt werden. Die Messungen wurden mit wasserverdünntem Blutserum durchgeführt, und zwar entweder mit einem konventionellen Flammenabsorptionsspektralphotometer oder unter Verwendung eines Resonanzmonochromators. Die Eichlösungen enthielten Natrium und Kalium mit annähernd den Konzentrationen, wie sie in den Serumlösungen vorliegen, da diese Metalle eine leichte Anregung der Lithiumabsorption verursachen. Die Ergebnisse sind bis auf ±0.2 µg Li/ml im Serum reproduzierbar. Die Empfindlichkeitsgrenzen betragen bei zehnfach verdünnten Proben 0.3 µg Li/ml mit dem konventionellen Instrument und 0.6 µg Li/ml mit dem Resonanzmonochromator.

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SEPARATION OF SOME ORGANIC MIXTURES BY FRACTIONAL ENTRAINMENT SUBLIMATION

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Sublimation has long been used as a method of separation or purification of organic compounds with appreciable vapor pressures. The use of this method has been restricted to situations where only one component of relatively high vapor pressure exists in the mixture, or to mixtures in which the components exhibit vastly different vapor pressures. Since there is no way to maintain a reflux condition in the sublimation process as there is in distillation, fractionation of samples which contain more than one volatile component is quite difficult if standard sublimation techniques are employed.

Using a horizontal tube sublimation apparatus, equipped with the provision for maintenance of a thermal gradient along the tube and a carrier gas entraining the sample at low pressures, BERG AND HARTLAGE were able to separate mixtures of various metal β-diketone chelates[1,2]. In this method, termed fractional entrainment sublimation, the sample is placed in the hot end of the sublimation apparatus, a thermal gradient is maintained along the tube and a stream of carrier gas is drawn across the sample at low pressures, about 1.0 mm of mercury.

Because these workers found that their products crystallized in high purity, and because the method required little in the way of sophisticated equipment, it seemed that fractional entrainment sublimation might be of significant value in both the isolation and purification of organic reaction products and in the analysis of organic compounds present in sublimable mixtures. The procedure proved to be of value for these applications; even tarry products of organic reactions yielded to this method of separation. While not as powerful as gas chromatography insofar as resolving power is concerned, many singular advantages are found.

EXPERIMENTAL

Apparatus

The basic apparatus described by BERG AND HARTLAGE was employed but some modifications were incorporated in the design. The changes included the addition of: (1) an integral brass condenser, (2) an auxiliary ring heater, (3) a second sublimator heating coil wound over the first, and (4) a constant temperature zone for the sample.

The modified design is illustrated in Fig. 1.

The sublimator inner-tube is a length of Pyrex or soft glass (Pyrex is more uniform) 120 cm in length and 1.20 cm O.D. The sublimator furnace tube is of brass 110 cm long, O.D. 1.50 cm, corresponding to an I.D. of 1.25 cm, and flared at each end. To this tube is brazed a brass condenser 15 cm long and 6 cm O.D., fitted with standard water inlet and outlet tubes. Brass thermometer wells, 0.6 cm I.D. by 4.0 cm long, were attached to the brass tube and spaced at the distances from the end of the tube as given below:

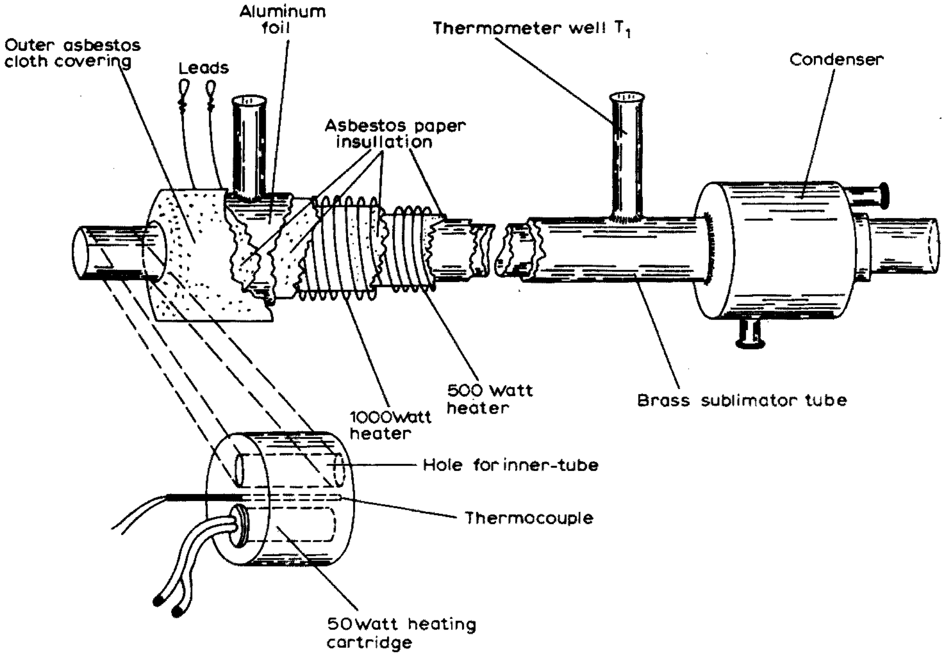

Fig. 1. The modified BERG–HARTLAGE sublimator.

Thermometer well number	T_1	T_2	T_3	T_4	T_5	T_6	T_7	(Condenser)
cm from end of tube	3	11	27	43	59	75	91	93–118

For electrical insulation, a 2-mm thick layer of asbestos paper was wrapped around the brass tube. To provide nearly linear temperature gradients for operation at either high or low maximum temperatures, 2 heating coils were installed. The first corresponded to approximately 500 W at 110 V, and was wound with 28-gauge nichrome wire with spacings of 5 turns per cm between T_1 and T_2; the number of turns per cm was then decreased in an approximately logarithmic manner to 0.5 turn per cm at T_7. This first element was covered with a 2-mm thickness of asbestos and the second heater, rated at 1000 W at 110 V, was wound with 20-gauge nichrome wire in the same manner as the first. The sublimator was then covered with heavy asbestos cloth until a radius equal to that of the condenser was obtained.

An auxiliary heater was constructed from a 3.5-cm segment of aluminum rod, 5.0 cm in diameter. This was fitted with a 50-W, 110-V heating cartridge and a chromel–alumel thermocouple. A 1.5-cm hole was drilled parallel to the heating cartridge to accommodate the glass inner-tube (Fig. 1). The temperature of the auxiliary heater was monitored by a 0–500° pyrometer.

The power supply for the sublimator heating elements and the auxiliary heater consisted of 2 powerstats. One, fused at 8 A, was used to power either of the 2 sublimator heaters; the other, fused at 2 A, powered the auxiliary heater.

The sample was contained in boats 12 × 6 × 1.5 mm made of aluminum foil. These were dried at 110° for 1 h and stored in a desiccator until used.

The flow of carrier gas (air) in the sublimator was controlled by regulating the pressure with an 8″ length of vacuum tubing pinched with a screw clamp to allow a pressure of 1.0 ± 0.2 mm mercury. This was positioned over the sample end of the glass inner-tube.

Calibration of both sublimator heaters and the auxiliary heater at various applied voltages was necessary to provide maximum flexibility of operation. Figure 2 illustrates typical thermal gradients observed along the sublimator under normal operating conditions, without the auxiliary heater.

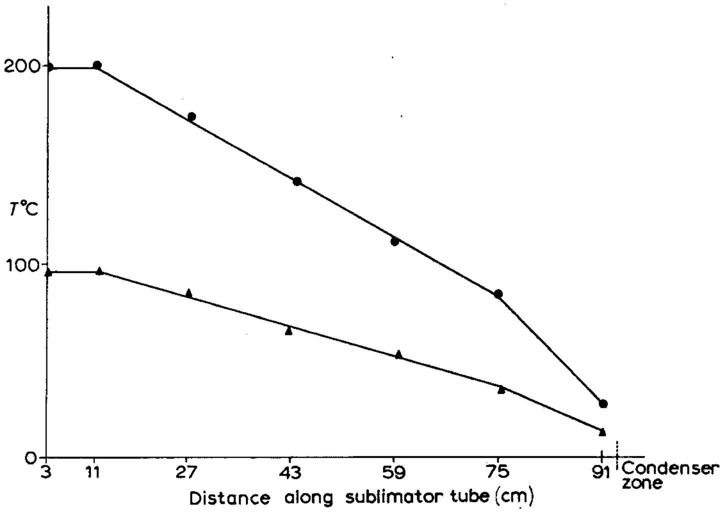

Fig. 2. Typical temperature gradients along the modified sublimator. (●) 1000-W heater at 55 V; (▲) 500-W heater at 55V.

Sublimation procedures

There are several ways of operating the sublimator. They are all applicable for either the high or the low (wattage) temperature sublimator heaters. These procedures are:

(*1*) *Normal operation.* This is the method of BERG AND HARTLAGE. The inner tube is positioned inside the sublimator and the sample is placed in this glass tube as near as possible to the T_1 thermometer well. The pressure controller is slipped in place over this end of the inner-tube. Vacuum is applied at the other (cool) end of the inner-tube. The powerstat is attached to either sublimator heating element, set at a predetermined voltage and turned on. Coolant is circulated through the condenser. After reaching the desired maximum temperature and its associated gradient, the sublimator is allowed to remain unchanged for the duration of the run. After 2 h, power to the heater and pump is cut, and the sublimator allowed to return to ambient temperature and pressure. The vacuum line and pressure controller are removed and the inner-tube withdrawn. Fractionated components are removed for further study by cutting the inner-tube and scraping them out, or washing them out with an appropriate solvent.

(2) *Operation with the auxiliary heater.* The sublimator is first preheated to the desired thermal gradient and maximum temperature. The inner-tube is inserted so as to leave at least 10 cm extended past the hot end of the sublimator. The sample is placed in the inner-tube at a point about 4 cm from the hot end of the sublimator. The auxiliary heater is positioned around the sample. The pressure controller is slipped into place, vacuum applied and the auxiliary heater rapidly raised to the desired temperature. The rest of the operation is performed as described above in procedure one.

(3) *Temperature-programmed operation.* In the temperature-programmed technique, the maximum temperature of the sublimator is increased constantly throughout the entire run. This method is used with or without the auxiliary heater.

Sublimation of pure reagents

The reagents used in these studies are listed in Table I. The melting points of the reagents were checked on a Fisher–Johns apparatus and all conformed to their respective literature values. Their ultraviolet and visible spectra were recorded on a Beckman DB spectrophotometer. The results of the fractional entrainment sublimation of the pure reagents are shown in Table I. The temperatures of the sublimation recrystallization zones were found by measuring the distance of the zones from the T_2 thermometer position, and referring to the temperature–distance curves as shown in Fig. 2. Provided that the pressure was the same (±0.3 mm), duplicate sublimations did not show zone temperature variations greater than ±2° for the leading (high temperature) edge. Approximately 10-mg samples were used. Each reagent was sublimed according to Procedure 1. Melting points of the sublimates and their UV

TABLE I

SUBLIMATION RECRYSTALLIZATION TEMPERATURE ZONES FOR SOME PURE ORGANIC COMPOUNDS AT SUBLIMATION PRESSURE OF 1 ± 0.2 mm MERCURY

Compound	*Sublimate zone (°C)*	*Compound*	*Sublimate zone (°C)*
Acetylsalicylic acid	20–15	Fluorenone	53–15
Dimeric-monothio-acetylacetone	25–20	Caffeine	60–25
		2-Nitrofluorene	70–45
Benzoic acid	30–15	Phenacetin	85–65
o-Nitroaniline	38–11	*p*-Nitroaniline	90–58
Fluorene	43–15	Anthracene	93–75
Dimeric-dithio-acetylacetone	47–37	*p*-Aminobenzoic acid	97–61
		2,5-Dinitrofluorene	108–78
Salicylic acid	48–32	2-Nitrofluorenone	110–85
m-Nitroaniline	52–40	2,7-Dinitrofluorene	125–110

TABLE II

SUBLIMATION DATA FOR VARIOUS SYNTHETIC MIXTURES AT 1 ± 0.3 mm MERCURY PRESSURE

Mixture components	*Sublimate zones (°)*	*Total weight (mg)*	*Best procedure (1000-W heater)*	*Temperature gradient T_2–T_7*	*Separation quality*
Benzoic acid and *p*-aminobenzoic acid	30–10 67–50	25.2	Normal procedure	156–15	Very good
Benzoic acid and salicylic acid	32–12 48–32	30.0	Auxiliary heater used	146–14	Fair
Acetylsalicylic acid, phenacetin and caffeine	20–14 85–60 60–30	20.0	Temp. prog. and auxiliary heater	150–14	Fair, good for phenacetin and aspirin
Dimeric dithioacetylacetone and dimeric monothioacetylacetone	49–30 25–19	13.4	Auxiliary heater	86–11[a]	Good
Fluorene and fluorenone	43–15 53–15	25.0	All procedures tried	74–14[a] (for proc. 1)	Some pure fluorenone
2-Nitrofluorene and 2-nitrofluorenone	71–20 110–80	50.4	Normal procedure	181–16	Good
Fluorene and 2-nitrofluorene	42–10 70–46	20.0	Auxiliary heater used	154–17	Good
Fluorenone and 2-nitrofluorenone	53–25 112–85	25.1	Auxiliary heater used	176–18	Very good
2,5-Dinitrofluorene and 2,7-dinitrofluorene	106–70 127–110	55.3	Auxiliary heater used	185–19	Good
o-Nitroaniline, *m*-nitroaniline and *p*-nitroaniline	40–13 52–42 90–60	27.6	Auxiliary heater with glass wool plugs	95–13[a]	Fair, some overlap of *o*- and *m*-isomers
Fluorene and anthracene	45–16 92–78	21.8	Normal procedure	151–16	Good

[a] The 500-W heating element was used for these attempts.

spectra were compared to the originals and indicated no decomposition in any of the sublimations.

Sublimation of mixtures

The synthetic mixtures fractionally sublimed, were of equal portions by weight. Sample weights were between 10 and 60 mg. The mixtures, weights, experimental conditions and results are summarized in Table II. Identification of the components was made on the basis of their temperature zones, melting points, and UV spectra.

Crude reaction products (Table III) were studied by the same procedure used to separate their analogous synthetic mixtures. The results of the sublimation of these products are also found in Table III.

TABLE III

SUBLIMATION DATA FOR SEPARATION OF VARIOUS CRUDE REACTION PRODUCTS AT 1 ± 0.3 mm MERCURY PRESSURE

Principal product	*Sublimate zone (°C)*	*Impurities isolated and detected*	*Sublimate zone (°)*
2-Nitrofluorene	75–46	2,7-Dinitrofluorene 2,5-Dinitrofluorene	132–108 95–83
2-Nitrofluorenone	118–83	Fluorenone	48–15
2,5-Dinitrofluorene	100–77	2,7-Dinitrofluorene 2-Nitrofluorene	130–100 76–15
Dimeric dithioacetylacetone	44–38	Dimeric monothioacetylacetone	27–20
Thio-thenoyltrifluoroacetone	~ 8 (condenser)	Two unidentified tars and other liquids	100–40

DISCUSSION

The determining factors involved in fractional entrainment sublimation are not very clear, but some empirical relationships can be noted. First, the greater the difference in the vapor pressures between the components the better the resolution. Secondly, the greater the differences in the molecular weight of the components, the better the separation; generally, higher molecular weight compounds give better results. Care must be taken in the separations, never to exceed the triple point temperature of the heavier molecular weight component. In the attempts at the resolution of the fluorene–fluorenone mixture, fluorenone has the lower triple point temperature, but a higher molecular weight than fluorene. When its triple point temperature was exceeded, a fog of liquid fluorenone formed in the sublimator and condensed on the surface of the fluorene sublimate which has the lower recrystallization zone temperature. Thus no complete resolution was ever achieved. In the case of the nitroaniline series, the triple point of the ortho-isomer can be exceeded since it has the lower zone temperature. It apparently does not tend to collect on the other members of the mixture.

The leading edge of the zones of sublimate (the highest temperature of the crystalline zone) is usually quite sharp and well defined. The first few centimeters of the zone usually contain the largest portion of the sublimate, usually as large crystals. The lower limit of the zone is often not as well defined. A low-power microscope is quite helpful in determining the trailing edge of the zone. The length of the zone depends to some extent upon the quantity of sample used, as well as the temperature gradient and the pressure of the sublimator. While samples of 10–60 mg were used in the work reported here, weights as high as 500 mg have been successfully separated, provided that the impurities were low, and that they crystallized at temperatures above the leading edge temperature of the desired constituent.

Good quality separations were achieved very often with the procedure described as *normal operation*. The use of the auxiliary heater for the rapid sublimation of the sample and the pre-heated sublimator sometimes enhanced the resolution of the sublimate zones. Separations also were helped in some cases by introducing a 2″ plug of loose glass wool on both sides of the sample boat. When these variations did not produce acceptable results, the sublimator tube was temperature-programmed. This method gave less reproducible results but usually increased the distance between the sublimate zones. The only good result with the aspirin, phenacetin and caffeine mixture was obtained this way. The explanation of the enhancement observed by using these modifications of the procedure is not clear. However, in most cases studied, when the sample was sublimed rapidly and introduced into the sublimator as close as possible to a single slug of vapor, resolution was enhanced. This may well hint at a differential migration process occurring in the sublimator.

The reproducibility of the leading edge temperature, even under different thermal gradients, indicates the possibility of using this temperature, as R_F values obtained in chromatography are used, for qualitative analytical purposes.

Another observation of note is the possibility of separating sublimable solids from tarry residues. Upon subjecting the tarry product of a thio-thenoyltrifluoroacetone synthesis to fractional sublimation, a zone of pure product was obtained as well as two bands of unidentified resinous impurities. The contaminants could not be removed by either recrystallization or the standard cold-finger sublimation techniques.

The resolution effects of the fractional entrainment sublimation technique, while admittedly not as powerful or as widely applicable as distillation or gas chromatography, seem to offer a rapid means of separation and identification of components of organic reaction product mixtures. The ease with which the separations, often apparently quantitative, may be obtained, makes the method worthy of consideration by the analytical and preparative organic chemist. The instrumentation is quite inexpensive, the products are obtained as solids which are sufficiently pure and in large enough quantity for most analyses, and the separations are obtained in two or less hours of unattended operation. No preparative steps are required for the sample other than possibly drying and weighing.

SUMMARY

Fractional entrainment sublimation has been successfully applied to mixtures of sublimable organic compounds. The components of the mixtures were obtained in well-defined crystalline zones, sufficiently pure for identification by melting points and spectroscopic analysis. The highest temperature limit of any zone was reproducible and may be comparable to the well known R_F value for qualitative analytical purposes. The technique was employed for the separation of 11 artificial mixtures and the purification of 5 crude reaction products. Samples of 10–60 mg were easily separated. The apparatus, operating procedures, and some of the factors which influence the separations are discussed.

RÉSUMÉ

La sublimation fractionnée par entraînement a été appliquée avec succès aux mélanges de composés organiques sublimables. Les composants des mélanges ont été obtenus en zones cristallines bien définies, à l'état suffisamment pur pour une identification à l'aide du point de fusion et au moyen de l'analyse spectroscopique. Ce procédé a été utilisé pour la séparation de onze mélanges artificiels et pour la purification de cinq produits de réaction.

ZUSAMMENFASSUNG

Die fraktionierte Sublimation unter Verwendung eines Trägergases wurde erfolgreich für Mischungen sublimierbarer organischer Verbindungen angewandt. Die Bestandteile der Mischungen wurden in gut definierten kristallinen Zonen erhalten und zwar auch ausreichend rein genug zur Identifizierung mittels der Schmelzpunkte und der spektroskopischen Analyse. Die höchste Temperaturgrenze irgendeiner Zone war reproduzierbar und ist mit dem bekannten R_F-Wert bei qualitativen analytischen Verfahren vergleichbar. Diese Technik wurde zur Trennung von 11 künstlichen Mischungen und zur Reinigung von 5 rohen Reaktionsprodukten verwendet. Proben von 10–60 mg wurden leicht getrennt. Die Apparatur, das Verfahren und einige Faktoren, welche die Trennungen beeinflussen, werden diskutiert.

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ABSORPTIOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM WITH RHODAMINE B

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The most sensitive reagent yet reported for the absorptiometric determination of uranium is the pyridylazo dye, PAR (4-(2-pyridylazo)resorcinol), whose uranium complex has a molar absorptivity of 39000 mmol^{-1} cm^2 at 530 nm[1]. A more sensitive determination based on a uranium–fluoride complex can be obtained by a fluorimetric method[2], but this is time-consuming. The detection limit for an absorptiometric method can be further lowered by the use of the highly absorbing complex of uranium with rhodamine B, the xantho dye tetraethylrhodamine.

The colour development was investigated for quantitative purposes on the basis of a spot test for uranium, using a benzene solution of rhodamine B and benzoic acid, described by FEIGL[3]. The optimum conditions for a stable colour, which lasts for at least an hour, were found to be given by the extraction of uranium(VI) into an organic reagent from a benzoate buffer at pH 4.5.

EXPERIMENTAL

Apparatus

A Zeiss spectrophotometer PMQ II with 1.000-cm quartz cells was used for the absorbance measurements.

Reagents

Benzoate buffer. This was prepared by dissolving 12 g of benzoic acid and 1 millimole of disodium ethylenediaminetetraacetic acid in 100 ml of 0.5 *N* sodium hydroxide solution, diluting to nearly 1 l with distilled water, adjusting the pH to 4.5 with 5 *M* nitric acid and making up to 1 l. Precipitated benzoic acid was removed by filtration after cooling.

Rhodamine B reagent solution. The reagent was made by adding 160 ml of organic solution I to 200 ml of diethyl ether and diluting to 1 l with organic solution II. Solution I was prepared by dissolving 4.5 g of benzoic acid in 200 ml of methyl isobutyl ketone; solution II was prepared by adding 1 g of rhodamine B ($C_{28}H_{30}N_2O_3 \cdot HCl$) to a separating funnel, containing 1 l of benzene and 1 l of water, shaking for 5 min, removing the water layer, and filtering the benzene layer through a paper filter. The final solution contained about 800 mg of rhodamine B per litre.

Standard uranium solutions. Five uranyl nitrate solutions were made by diluting aliquots of a standard solution, whose uranium concentration had been determined gravimetrically.

Recommended procedure

Pipette 3.00 ml of the nearly neutral sample solution, containing 0.02–3 μg uranium per ml into a 10-ml stoppered test tube. (Acid solutions should be neutralized beforehand by adding a drop of 0.1% bromophenol blue and adjusting the pH to 4.5 with 2 *N* sodium hydroxide solution till the blue colour appears.) Add 2.00 ml of benzoate buffer and 5.00 ml of the organic reagent. Mix the solutions by shaking for 2 min. Centrifuge the tube for 1 min. Measure the absorbance of the organic layer in a 1-cm cell against a reagent blank at 555 nm.

RESULTS AND DISCUSSION

Dissolved rhodamine B exists in the colourless lactone form and the red quinonoid form. The latter is suppressed by hydroxyl ions and organic electron donors such as ethers. Preliminary investigations showed the existence of a 1:1 uranium–rhodamine B complex in benzene–diisopropyl ether, which has a red-orange fluorescent colour and has its maximum absorption at 555 nm. The presence of benzoic acid in the organic layer intensifies the colour, but excess hydroxonium ions inhibit the complex formation. The optimum pH value for the chosen volume ratio of organic to aqueous liquid was found to be 4.5, which can be maintained by a benzoic acid–sodium benzoate buffer; this buffer also guarantees a high concentration of benzoic acid in the organic layer. EDTA was added to the buffer to complex interfering metals, particularly iron. Some methyl isobutyl ketone was added to the organic reagent to improve the separation of the layers after the extraction. The absorbance curves for the reagent blank and the uranium complex measured against water are shown in Fig. 1.

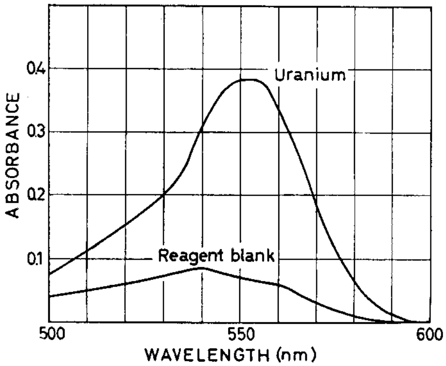

Fig. 1. Absorption spectra of the uranium–rhodamine B complex and the reagent blank.

Six determinations on each of the 5 standard uranium solutions and 10 determinations without uranium present were carried out as described in the recommended method. The series of absorbances at about 0.06, 0.11, 0.17, 0.27, 0.47 and 0.89, measured against water, corresponded to the uranium amounts 0, $2\cdot10^{-6}$, $5\cdot10^{-6}$, $1\cdot10^{-5}$, $2\cdot10^{-5}$ and $4\cdot10^{-5}$ mg-atom respectively. The calibration graph of the absorbance, measured against a reagent blank, as a function of the amount of uranium should be a straight line, the slope of which is related to the molar absorptivity.

Linear regression analysis[4] of the available data gave a line through the origin as the best fit. The molar absorptivity of the complex, measured under the experimental conditions described, is 102700 mmol^{-1} cm^{2}. The error in this figure, expressed as the relative standard deviation, is 0.28%. The variances within the series of absorbance measurements are $1 \cdot 10^{-6}$ for the 2 lowest absorbance levels and $20 \cdot 10^{-6}$ for the others. The residual variance of the data along the calibration line of $7 \cdot 10^{-6}$ can be attributed to the measurement error; this means that the Lambert–Beer laws are followed in the range of uranium amounts investigated[5].

The detection limit of the proposed method is 0.02 μg per ml at the 99% confidence level[6]. Calculations show that the relative standard deviations for unknown samples, determined by means of the calibration graph, can be estimated to be 20 %, 2% and 0.6% for uranium concentrations of 0.02 μg, 0.2 μg and 3 μg per ml respectively.

The addition to the uranium solution of $2 \cdot 10^{-6}$ moles of EDTA as a component of the buffer solution prevents several metal ions from influencing the determination of uranium. The ions mentioned in Table I were studied. No interference was observed if the ions were present in amounts less than $2 \cdot 10^{-6}$ g-ion. The molar absorptivities of the rhodamine B complexes at 555 nm when larger amounts were added, are given in Table I. The complexes have a violet-red colour, except these with lead and aluminium, which show the same red-orange fluorescent colour as the uranium complex.

TABLE I

STUDY OF INTERFERENCES

Ion	*Molar absorptivity*[a]	*Ion*	*Molar absorptivity*[a]	*Ion*	*Molar absorptivity*[a]
Ag^{+}	—	Cu^{2+}	150[b]	Pb^{2+}	610
Al^{3+}	350	Fe^{2+}	240[b]	Rb^{2+}	—
Au^{3+}	340[b]	Fe^{3+}	2000[b]	Ru^{3+}	—
Ba^{2+}	—	Ga^{3+}	360[b]	Sb^{3+}	—[b]
Bi^{3+}	—[b]	Hg^{2+}	860[b]	Sr^{2+}	—
Ca^{2+}	—	Mg^{2+}	—	Tl^{3+}	—
Ce^{3+}	—	Mn^{2+}	—	Th^{4+}	700[b]
Co^{2+}	—	MoO_4^{2-}	—	Zn^{2+}	50
Cr^{3+}	1000	Ni^{2+}	—	Zr^{4+}	—[b]

[a] In mmol^{-1} cm^{2}.

[b] Precipitation with large amounts.

SUMMARY

Uranium(VI) can be extracted as a complex with rhodamine B into a benzene–ether–hexone solvent from a benzoate buffered solution. Optimum conditions for the colour development are defined, leading to a molar absorptivity of 102700 mmol^{-1} cm^{2} at 555 nm, the highest yet reported for a uranium complex. The determination of uranium in the range 0.02–3 μg/ml in nitrate samples is described. The relative standard deviation ranges from 20 to 0.6%. The interference of several ions is investigated.

RÉSUMÉ

L'uranium(VI) peut être extrait sous forme d'un complexe avec la rhodamine B dans le benzène–éther–hexone comme solvant, en tampon benzoate. On décrit une méthode de dosage de l'uranium (0.02–3 µg/ml) dans des échantillons de nitrate. Déviation standard relative de 20 à 0.6%. On examine l'influence de plusieurs ions.

ZUSAMMENFASSUNG

Uran(VI) kann als Rhodamin-B-Komplex mit Benzol–Äther–Hexon aus benzoatgepufferter Lösung extrahiert werden. Unter den optimalen Bedingungen für die Farbentwicklung ergab sich eine molare Absorption von 102 700 mmol^{-1} cm^{2} bei 555 nm. Das ist der bisher höchste angegebene Wert für einen Urankomplex. Die Bestimmung von Uran im Bereich von 0.02–3 µg/ml in Nitratproben wird beschrieben. Die relative Standardabweichung liegt zwischen 20–0.6 %. Störungen verschiedener Ionen werden untersucht.

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DETERMINATION OF HYDROXYLAMINE WITH NESSLER REAGENT*

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Nessler reagent has long been the standard reagent for the determination of ammonia, by colorimetric assay of the yellow complex, $HgI_2 \cdot HgNH_2I$, formed in alkaline solution[1]. It is known that volatile aliphatic amines[2] and guanidine[3] also react with Nessler reagent, and that aldehydes interfere by reducing Nessler reagent to produce a mercury precipitate[4]. Although the latter reaction has been used as a spot test for aldehydes[5], there is no mention of any reaction between Nessler reagent and hydroxylamine in common compilations of analytical chemistry[6,7]. In the course of studies on the hydrolysis of hydroxyurea ($H_2N{-}CO{-}NHOH$) by urease[8], it was found that hydroxylamine forms a potent color complex with Nessler solution. Subsequently, hydroxylamine was also found to be measured by the ninhydrin reagent for ammonia. This reactivity will be of importance when analyses of ammonia, hydroxylamine, and hydroxamic acids are to be carried out in the presence of one another. An example of this is the determination of the stoichiometry of hydroxyurea hydrolysis, where a hydroxamic acid is converted to hydroxylamine, ammonia, and carbon dioxide[8]. The several compounds were therefore tested by a series of colorimetric procedures to determine their analytical specificity, so that one might select a method in accordance with the mixture of compounds present. In addition, the nature of the hydroxylamine reaction with ammonia reagents was studied by subsequent assay for residual hydroxylamine and nitrite, and a simple adaptation of Nessler reagent was developed to provide a new assay for hydroxylamine.

EXPERIMENTAL

Reagents

Ammonium sulfate was used as the ammonia source. Hydroxylamine hydrochloride was recrystallized 3 times from ethanol, after which 98% purity was established by titration, following reduction to ammonia with alkaline iron(II) sulfate in a Kjeldahl apparatus and steam distillation into boric acid. Reagent-grade hydroxylamine hydrochloride may assay as much as 30% low by this method after several months standing, probably because of its hygroscopicity. Fresh 10 m*M* hydroxylamine solutions were prepared each day, since decomposition was fairly rapid at this concentration (about 50% loss in 3 days). Hydroxyurea was obtained from the

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Cancer Chemotherapy National Service Center (NSC No. 32065) through Dr. PAUL CARBONE. Acetohydroxamic acid and propionohydroxamic acid were prepared as previously described[8] and found to be more than 98% pure by neutralization equivalent and paper chromatography. N-Hydroxyurethane (technical grade) was purchased from the Aldrich Chemical Co., Milwaukee, Wisconsin. All other compounds used were of reagent grade.

Methods

All colorimetric assays were performed in a prism-spectrophotometer using 1-cm quartz cells. Ammonia was measured with Nessler reagent without preliminary volatilization and at a final alkali concentration of approximately 0.05 *M*[9]. The ninhydrin method of MOORE AND STEIN was also used to measure ammonia[10]. Hydroxyurea was measured by the picryl chloride procedure[11] and by the method of DAVIDSON AND WINTER[12]. Aceto- and propionohydroxamic acids were measured in acid iron(III) chloride[8,13]. Hydroxylamine was measured by thioester trapping[8], and by sulfanilic acid-α-naphthylamine diazotization and coupling[14,15]. The latter procedure was performed without the preliminary acid hydrolysis used to liberate "bound" hydroxylamine (*i.e.* oximes and hydroxamic acids), since variable decomposition of hydroxylamine itself was found after such treatment. When the initial oxidation step with iodine and subsequent addition of sodium arsenite are omitted, this procedure becomes the familiar GRIESS test for nitrites[16].

RESULTS AND DISCUSSION

Hydroxylamine was found to give a color reaction with the ninhydrin solution reaction of MOORE AND STEIN[10]. In this system, the molar absorptivity is approximately the same for hydroxylamine and ammonia, and it is reasonable to assume that hydroxylamine is reduced by the tin(II) chloride present in the solution, and is measured as ammonia.

In the Nessler reaction, hydroxylamine has a molar absorptivity more than 5-fold that of ammonia. This means that reduction of hydroxylamine and measurement as the ammonium mercuriiodide complex is not the explanation for this color reaction, although the absorption spectra of Nessler reagent with ammonia and with hydroxylamine are essentially the same. Despite the high molar absorptivity, the colorimetric assay of hydroxylamine with Nessler reagent under the usual conditions has limited utility because concentrations yielding an absorbance of 0.200 or more result in precipitation. A reasonable explanation for this would be the oxidation of hydroxylamine to nitrite and reduction of the Nessler reagent to an insoluble state, in a manner analogous to the reaction occurring with aldehydes[4].

To investigate this possibility, colorimetric assays for hydroxylamine[14,15] and for nitrite[16] were performed on these compounds in the presence and absence of prior treatment with Nessler reagent. The results are summarized in Table I. Nessler reagent had no absorption in these assays, and nitrite produced no absorbance or precipitate in Nessler reagent. The precipitate produced by this concentration of hydroxylamine (0.1 m*M*) in Nessler reagent redissolved upon dilution in the sulfanilic acid of the CZAKY[15] and GRIESS[16] tests so that no intermediate step was necessary in applying this assay sequence. It is clear from Table I, that approximately half of the

TABLE I

ABSORPTION OF HYDROXYLAMINE AND NITRITE IN THE CZAKY AND GRIESS TESTS WITH AND WITHOUT PRIOR NESSLERIZATION

(Optical density was measured at 525 nm for 10 μM final concentration of the reactants)

		Czaky test for hydroxylamine as nitrite	*Griess test for nitrite*
NH_2OH	Direct	0.245	0.000
	After Nesslerization	0.125	0.325
HNO_2	Direct	0.255	0.660
	After Nesslerization	0.240	0.600
Nessler reagent		0.000	0.000

hydroxylamine was recovered as nitrite after Nesslerization, indicating that a redox reaction between hydroxylamine and Nessler reagent does occur, and was probably responsible for the precipitation phenomenon. In a series of experiments with varying concentrations of hydroxylamine, recovery as nitrite after Nesslerization ranged from 45–70% but was never complete. The remainder could not be identified as free hydroxylamine, since the preliminary oxidation step in the CZAKY procedure failed to increase the yield of nitrite from hydroxylamine after Nesslerization. It is therefore possible that the remaining hydroxylamine was tightly bound in a mercuriiodide complex analogous to that formed with ammonia and which is responsible for the marked absorbance produced by low concentrations of hydroxylamine. This possibility is supported by the fact that changing the pH of the Nessler reaction converted this procedure to a specific hydroxylamine assay suitable for use over an 8-fold range of optical densities. The exact Nesslerization procedure found to be most useful for hydroxylamine assay is given below.

Recommended method for determination of hydroxylamine

Dilute one part of concentrated Nessler reagent (Fisher Chemical Company), at the time of use, with one part of water and $4\frac{2}{3}$ parts of 2.5 *N* sodium hydroxide. Mix the solution containing hydroxylamine, at a concentration of 0.1–1 m*M*, with an equal volume of 4% perchloric acid. After centrifugation to remove protein (if applicable), add 0.6 ml of this solution to 4.7 ml of water plus 0.2 ml of the diluted Nessler reagent. After standing for 2 min, during which time precipitation occurs, add 0.5 ml of *N* hydrochloric acid with mixing. Over the subsequent 60 min, the precipitate dissolves and color formation reaches its maximum level. Read the solutions at 420 nm, along with a set of identically treated standards.

Under these conditions the molar absorptivity is 7500 for final hydroxylamine concentrations of 5–50 μM, while ammonium salts give no absorbance at concentrations as high as 400 μM, the ammonium mercuriiodide complex being decomposed upon addition of the hydrochloric acid. It is essential that the acid be added after Nesslerization, and not before, to provide a satisfactory assay for hydroxylamine.

It is clear from the above that the presence of hydroxylamine must be taken into account in any determination of ammonia based on reaction with Nessler reagent or ninhydrin. Since hydroxylamine has a relatively low vapor pressure, it will not interfere with ammonia determinations involving preliminary volatilization of ammonia from alkaline solutions, as commonly employed in clinical laboratories[17-19], and an assay of this type was used successfully for the measurement of ammonia released during hydroxyurea hydrolysis[8].

Since the hydroxamic acids have not been tested in colorimetric methods for ammonia, hydroxyurea, and nitrite, their reactivity in these assays was determined, and is summarized in Table II, together with that of the compounds discussed above. In contrast to hydroxylamine, the hydroxamic acids produced no color reaction in Nessler reagent. Propionohydroxamic acid gave essentially the same results as acetohydroxamic acid in all assays and is therefore omitted from Table II. Ammonium salts produced no absorption in the colorimetric assays for hydroxylamine and nitrite. Should contamination with any of these products be suspected or anticipated during assay of another constituent, its presence may be established by introducing an appropriate second assay from Table II.

SUMMARY

Hydroxylamine forms strong color complexes with ninhydrin and Nessler solution, two of the standard reagents for ammonia. In the case of ninhydrin, ammonium salts and hydroxylamine have the same molar absorptivity; hydroxylamine is probably reduced to ammonia and measured as such. With Nessler reagent, hydroxylamine has 5 times the molar absorptivity of ammonia at low concentrations; levels above 10 *µM* result in reagent precipitation, because of a redox reaction involving oxidation of hydroxylamine to nitrite and reduction of Nessler reagent. The conditions of Nesslerization can be altered to provide a specific assay for hydroxylamine in the range of 5–50 *µM*, with no absorbance being produced by ammonium salts. Other hydroxylamine derivatives give no color reactions with ninhydrin or Nessler reagent.

RÉSUMÉ

L'hydroxylamine donne des complexes fortement colorés avec la ninhydrine et la solution de Nessler, deux des réactifs de l'ammoniaque. Dans le cas de la ninhydrine, les sels d'ammonium et l'hydroxylamine ont la même absorption molaire; l'hydroxylamine est probablement réduite en ammoniaque et mesurée sous cette forme. Les conditions de "nesslerisation" peuvent être modifiées pour obtenir une réaction spécifique de l'hydroxylamine (5–50 *µM*), sans absorption due aux sels d'ammonium. Les autres dérivés de l'hydroxylamine ne donnent pas de réactions colorées avec la ninhydrine ou le réactif de Nessler.

ZUSAMMENFASSUNG

Hydroxylamin bildet stark gefärbte Komplexe mit Ninhydrin und Nesslerschem Reagenz. Ninhydrin besitzt für Ammoniumsalze und Hydroxylamin die gleiche molare Absorption. Hydroxylamin wird wahrscheinlich zum Ammonium reduziert und als solches gemessen. Mit Nesslerschem Reagenz ergibt Hydroxylamin

TABLE II

APPROXIMATE MOLAR ABSORPTIVITIES OF VARIOUS NITROGEN COMPOUNDS IN DIFFERENT METHODS

Methods and reference	*Ammonia* (NH_3)	*Hydroxylamine* (NH_2OH)	*Hydroxyurethane* ($C_2H_5O(CO)NHOH$)	*Hydroxyurea* ($H_2N(CO)NHOH$)	*Acetohydroxamate* ($CH_3(CO)NHOH$)	*Nitrite* (HNO_2)	*Urea* ($H_2N(CO)$-NH_2)
$FeCl_3$[13,8]	<10	<10	<10[a]	<60[a]	1,000	<10	<10
K_2HgI_4 (Nessler)[9]	2,000	11,000	<20	<20	<20	<20	<20
Sulfanilic acid–α-naphthylamine[16]	<600	<600	<100	<100	<100	60,000	<100
Iodine sulfanilic acid–α-naphthylamine[15]	40	24,500	32	2	42	24,500	2
Acetylthioacetate[8]	<10	775	<10[a]	<75[a]	775	<10	<10
Picryl chloride[11]	—	<100	—	1,700	<150	—	<10
Diacetyl monoxime[11]	<50	<200	<100	50,000	$<1,000$	—	55,000
Urease-diacetyl monoxime[12]	<50	<200	<100	50,000	$<1,000$	—	<100
Ninhydrin[10]	4,000	4,000	—	—	<400	—	—

[a] Strong initial color reactions fade rapidly. The values given are based on assay after 30-min standing.

bei niedrigen Konzentrationen die fünffache molare Absorption. Mehr als 10 μM ergeben im Reagenz einen Niederschlag, da das Hydroxylamin zum Nitrit oxydiert und das Nesslersche Reagenz reduziert wird. Durch geänderte Reaktionsbedingungen kann eine spezifische Probe für Hydroxylamin im Bereich von 5–50 μM geschaffen werden, wobei keine Absorption durch Ammoniumsalze erzeugt wird. Andere Hydroxylamin-Derivate ergeben keine Farbreaktionen mit Ninhydrin oder Nesslerschem Reagenz.

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THE DETECTION OF OXYGEN IN ORGANIC COMPOUNDS WITH POTASSIUM TETRATHIOCYANATO-COBALTATE(II)

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Several tests are available for the detection of oxygen in organic compounds but, unlike those for other elements, none is entirely satisfactory; either the techniques are complicated or the tests are not reliable enough and have many exceptions.

Among the methods quoted in texts dealing with qualitative organic analysis books[1] are a microqualitative adaptation[2] of UNTERZAUCHER's quantitative method[3] in which the sample is vaporized at 950–1000° in a stream of pure nitrogen and the products carried over pure carbon heated to 1100–1500°, the carbon monoxide being identified with iodine pentoxide. The commonest test is the ferric thiocyanate test[4] which is based on the insolubility of this compound in hydrocarbons and halogen derivatives so that no red colour appears; this test is performed on liquid samples or on solids dissolved in benzene or carbon tetrachloride, the reagent being added in solid form or impregnated on a paper. The method has many limitations: several oxygen-containing compounds (some ethers and esters) do not give the colour, whereas most sulphur and nitrogen compounds do give it; oxygen-containing solids that are not sufficiently soluble in benzene or carbon tetrachloride give negative tests; and the reactivity of iron(III) with some organic compounds is an unavoidable interference.

In the present work the use of a potassium cobalt-thiocyanate complex (potassium tetrathiocyanato-cobaltate(II)) is proposed for identifying oxygen in organic compounds. The preparation and use of this reagent were studied as well as the behaviour of a number of organic compounds covering a wide range of organic functions.

The blue color of cobalt thiocyanate in some organic solvents, initially employed by VOGEL[5] for the identification of cobalt(II), has found other analytical applications. For example, cobalt can be determined colorimetrically without previous extraction, employing water-miscible solvents such as acetone and ethyleneglycol[6]; in the Weber test, the color is used to distinguish isobutyl alcohol from isoamyl alcohol and both from their acetic esters[7]. It has also been employed in a systematic study of technical solvents to detect the oxygen-containing ones[8]. All these previous works indicated that the present study of the behaviour of all organic functions would be worthwhile.

EXPERIMENTAL

Reagent preparation

Preliminary tests indicated that the reagent was best used in the solid state, being easier to handle and more effective than the corresponding aqueous potassium thiocyanate and cobalt(II) solutions. Moreover, the test can then be applied to solid organic materials, insoluble in water or organic solvents, working at their melting temperature.

A reagent of suitable quality is prepared as follows. Stoichiometric amounts of cobalt sulfate and potassium thiocyanate are intimately ground in a mortar. The mixture obtained is extracted with ethanol, potassium sulfate remaining insoluble. The filtered alcoholic extract is slowly evaporated on a water bath and the blue prismatic needles obtained are dried over calcium chloride.

Analysis of the complex

Quantitative analysis suggested the formula $K_2Co(SCN)_4 \cdot 4\,H_2O$. (Calculated: Co, 13.3%; K, 17.7%; C, 10.8%; N, 12.7%; H, 1.8%; S, 29.0%. Found: Co, 13.2%; K, 17.9%; C, 10.8%; N, 12.9%; H, 1.7%; S, 28.2%.)

Test techniques

Two techniques are proposed depending on whether the organic material is a liquid or a solid.

Liquid materials. Place in a small test tube 0.5–1.0 ml of the compound under analysis and add about 10 mg (a knife tip) of the reagent. The liquid quickly becomes an intense blue when the test is positive. If it is negative, the reagent remains insoluble or changes its appearance.

Solid materials. Place on a perfectly clean microscope slide, about 50 mg of the compound under test and 3–5 mg of reagent. Heat carefully over the flame of a microburner until a temperature slightly above the melting point is reached. The molten mixture becomes intense blue when the test is positive; otherwise, the reagent remains insoluble in the fused material or changes its appearance.

Compounds tested

To obtain the widest knowledge possible about the applicability of the test, about 500 compounds with organic functions chosen among the most common were tested. Some uncommon or new compounds were also tested; for instance, some aromatic chlorocarbons synthesized by BALLESTER *et al.*[9] and some dinitriles, iminodioximes and isonitrosoacetyl derivatives prepared by ourselves for other purposes.

Analysis of the complexes given with some primary amines

In order to elucidate the observed reaction with some primary amines, the insoluble residues produced in the tests were analysed. The aniline and butylamine complexes were analysed as examples of aromatic and aliphatic amines.

The quantitative results obtained were as follows. The aniline complex corresponded to the formula $Co(SCN)_2(C_6H_5NH_2)_2$. (Found: N, 15.6%; S, 17.6%; C, 46.0%; Co, 15.9%; H, 3.5%. Calculated: N, 15.5%; S, 17.7%; C, 46.5%; Co, 16.3%; H, 3.8%.) The butylamine complex corresponded to the formula $Co(SCN)_2(C_4H_9NH_2)_2$. (Found: N, 17.5%; S, 17.7%; C, 36.7%; Co, 14.8%; H, 6.5%. Calculated: N, 17.4%; S, 18.5%; C, 37.0%; Co, 15.2%; H, 6.8%.)

DISCUSSION AND RESULTS

The compounds tested are listed in Table I (negative tests) and Table II (positive tests). From these data, the following conclusions can be drawn.

TABLE I

COMPOUNDS CONTAINING NO OXYGEN (NEGATIVE TEST)

Hydrocarbons

n-Pentane
n-Hexane
n-Heptane
n-Octane
n-Nonane
n-Decane
n-Undecane
n-Dodecane
2,4-Dimethylpentane
2,4-Dimethylhexane
2-Methylbutane (isopentane)
2,3-Dimethylbutane
Cyclopentane
Cyclohexane
1,3-Cyclopentadiene
Cyclopentene
Cyclohexadiene
Dicyclopentadiene
Paraffin
Allylbenzene
1-Heptine
α-Pinene
Benzene
Toluene
Ethylbenzene
p-Xylene
o-Xylene
m-Xylene
1,3,5-Trimethylbenzene (mesitylene)
Indane
1,2,3,4-Tetrahydronaphthalene (tetralin)
Naphthalene
Dibenzyl
Diphenyl
Trimethylmethane
Phenanthrene
Anthracene
Isopropylbenzene (cumene)
Decalin
Phenylacetylene
2-Phenylpropene
Stilbene
1,1-Diphenylethylene
1,4-Diethylbenzene
2,5-Diethyltoluene
2-Methylindane
Indene
Propylbenzene
p-Cymene

Halogenated compounds

Trichloromethane
Dichloromethane
1,1,2-Trichloroethylene
1,2-Dichloroethane
1,1-Dichloropropane
1,2-Dichloropropane
Tetrachloromethane
1,2-Dichloroethylene
Chloroethane
Tetrachloroethylene
Tribromomethane
Dibromomethane
Bromoethane
Bromoethene
2-Bromopropane
1-Bromopropane
Bromopentane
Bromobutane
1,3-Dibromopropane
Chlorobenzene
1,2-Dichlorobenzene
2-Chlorotoluene
Trichlorobenzene
Bromobenzene
1,4-Dibromobenzene
1,2-Dibromopropene
1-Bromo-2-chlorobenzene
Triiodomethane
Iodomethane
2-Iodopropane
1,2-Diiodoacetylene
2-Chloronaphthalene
2,3-Dichloronaphthalene
2-Chlorobiphenyl
2,4,6-Trichlorotoluene
1,2-Dibromocyclohexane
Tetrachloronaphthalene
Dichloroacetylene
Benzyl chloride
Benzyl bromide
Perchloroindane
1,2-Dibromoethane
H-Heptachlorotoluene
α H-Undecachlorodiphenylmethane
α H, α′ H-Octachloro-*m*-xylene
α H, α′H-Octachloro-*p*-xylene

Sulfur compounds

Allyl sulfide
Ethyl vinyl sulfide
Carbon sulfide
Methylphenyl sulfide
Methylbenzyl sulfide
1,2-Ethanedithiol
1,2-Propanedithiol
1,3-Propanedithiol
Dodecyldecanethiol

Amines

(*a*) *Primary*

Propylamine
Butylamine
Aniline
Isobutylamine
Ethylenediamine
o-Toluidine
1-Naphthylamine
p-Chloroaniline
o-Chloroaniline
2,5-Dichloroaniline
m-Toluylenediamine
Benzylamine

(*b*) *Secondary and tertiary*

N-Butylaniline
N,N-Diethylaniline
Diphenylamine
N,N-Diphenylbenzidine
N-Methylaniline[a]
N-Ethylaniline[a]
Diethylamine[a]
N-Ethyl-*m*-toluidine[a]
N-Propylaniline[a]
Trimethylamine[a]
Triethylamine
N,N-Dimethylaniline[a]

Heterocycles

Pyrrole
Pyrrolidine
Pyridine
Piperidine
Quinoline
Thiophan
Thiophen

---

[a] A green colour was obtained.

(*a*) All oxygen-containing organic compounds (alcohols, aldehydes, ketones, acids, esters, ethers, phenols, nitro and nitroso derivatives, amides, imides, heterocycles, etc.) rapidly give positive tests (blue color) with potassium thiocyanatocobaltate(II). The only compounds which do not contain oxygen but which give positive tests are nitriles.

(*b*) All other compounds containing no oxygen (hydrocarbons, halogen and sulphur derivatives, azo compounds, heterocyclic compounds and amines) give negative tests.

(*c*) Among all the oxygen-containing compounds tested, only 2 gave negative tests: thymol and furan. The cause of this irregularity may be, in the latter case, the special character of the oxygen atom in the furan ring, for tetrahydrofuran gives a positive response to the test. The participation of the unshared electron pairs of the furan oxygen atom in the aromatic nature of the ring is also evidenced by other well-known physical and chemical effects.

For thymol, the negative reaction may be explained by a steric effect which hinders solvation; unlike thymol, its isomer carvacrol gives a weak positive reaction. This interpretation is confirmed by the fact that another sterically hindered phenol, di-*tert.* butyl-*p*-cresol, which is so sterically hindered that it has lost the characteristic solubility of phenols in alkalies, also gives a negative test.

(*d*) Some primary amines, though behaving normally, *i.e.* giving no blue color, react with the cobaltothiocyanate to yield other complexes with amine ligands instead of thiocyanate ligands. This was shown by the quantitative analysis of the insoluble residues, with different colours, obtained in the tests with aniline and butylamine.

(*e*) Some secondary and tertiary amines such as methylaniline, ethylaniline and dimethylaniline give weak green shades.

(*f*) Oxygen-containing organic compounds which are themselves reagents for the cobalt(II) ion, do not give positive tests and give their characteristic colorations or precipitates. This is the case with α-nitroso-β-naphthol, isonitrosoacetanilides, imidodioximes, etc.

(*g*) The test cannot be applied to materials melting with partial decomposition.

SUMMARY

A new micro or semimicro test for detection of oxygen in organic compounds is based on the blue colour given on treatment with a solid potassium thiocyanatocobaltate reagent. The test was checked with *ca.* 500 compounds containing various functional groups; very few anomalous reactions were observed.

RÉSUMÉ

On propose une nouvelle réaction (micro et semimicro) pour l'identification de l'oxygène dans des composés organiques; elle est basée sur la coloration bleue obtenue au moyen du thiocyanatocobaltate de potassium. Environ 500 substances renfermant divers groupements fonctionnels ont été essayées; on n'observe que de très rares anomalies.

TABLE II

OXYGEN-CONTAINING COMPOUNDS AND NITRILES (POSITIVE TEST)

Alcohols
Methanol
Ethanol
1-Propanol
2-Propanol
1-Butanol
1-Pentanol
1-Heptanol
1-Octanol
1-Decanol
Isobutanol
t-Butanol
2-Pentanol
3-Pentanol
1-Hexanol
Isooctanol
Cyclohexanol
Benzyl alcohol
Dodecanol
Tetradecanol
Hexadecanol
Octadecanol
Heptadecanol
Pentadecanol
2,3-Dibromopropanol-1
Methylcyclohexanol
3-Chloropropanol-1
1-Nonanol
1,3-Propanediol
Citronellol
Geraniol
1,2-Butanediol
Cyclopentanol
Pinacol
Terpineol
Cinnamyl alcohol
Menthol
Diphenylcarbinol
Cholesterol
2-Ethyl-1-hexanol
3-Methylcyclohexanol

Aldehydes
Acetaldehyde
Propanal
Glyoxal
Butanal
Chloroacetaldehyde
Decanal
Dodecanal
Hexadecanal
Paraldehyde
Benzaldehyde
Phenylacetaldehyde
Salicylaldehyde
Citronellal
p-Chlorobenzaldehyde
Citral
Acetylsalicylaldehyde
2-Methoxybenzaldehyde
Cinnamaldehyde
p-Nitrobenzaldehyde
4-Bromobenzaldehyde
Terephthalaldehyde
2,4-Dihydroxybenzaldehyde
Naphthaldehyde
Chloral hydrate

Carboxylic acids
Formic
Acetic
Propionic
Butyric
Pentanoic
Methoxyacetic
Hexanoic
Decanoic
Nonanoic
Heptanoic
Isopentanoic
Oleic
Isobutyric
Citric
Oxalic
Malonic
Acetylsalicylic
Benzoic
3-Nitrosalicylic
Salicylic
o-Aminobenzoic
p-Aminobenzoic
Hippuric
Malic
Cinnamic
p-Nitrobenzoic
p-Methoxybenzoic
Phthalic
Camphoric
Phenylacetic
o-Bromobenzoic
Succinic
3,5-Dinitrobenzoic
Glutamic
Ascorbic
4-Amino-1-naphthoic
Mandelic
Adipic
Glutaric
o-Toluic
Undecylenic

Anhydrides and acid halides
Acetic anhydride
Propionic anhydride
Phthalic anhydride
Cinnamic anhydride
Maleic anhydride
Acetyl chloride
Oxalyl chloride
Benzoyl chloride
Propionyl chloride
Benzoyl bromide
Acetyl bromide
Butyryl chloride
p-Nitrobenzoyl chloride

Esters
Methyl formate
Ethyl formate
Butyl formate
Isobutyl formate
Methyl acetate
Ethyl acetate
Isopropyl acetate
Butyl acetate
Pentyl acetate
Isobutyl acetate
Isopentyl acetate
Propargyl acetate
Methyl propionate
Ethyl propionate
Isopropyl propionate
Ethyl butyrate
Ethyl isobutyrate
Dimethyl oxalate
Diethyl oxalate
Ethyl lactate
Ethyl pyruvate
Diethyl malonate
Methyl salicylate
Ethyl salicylate
Methyl benzoate
Ethyl cinnamate
Methyl cinnamate
p-Cresyl benzoate
Ethyl benzoate
Ethyl cyanoacetate
Phenyl salicylate
Ethyl acetoacetate
Diethyl adipate

TABLE II (Continued)

Esters

- Phenyl benzoate
- Methyl stearate
- Ethyl-*p*-nitrocinnamate
- Glyceryl monostearate
- Glyceryl tristearate
- Glyceryl tripalmitate
- Methyl 2-aminobenzoate
- Ethyl 2-aminobenzoate
- Diethyl phthalate
- Diisobutyl phthalate
- Ethyl chloroacetate
- Ethyl *p*-aminobenzoate
- Methyl cyanoacetate
- Ethyl bromoacetate
- Methyl phenylacetate
- Methyl 2-hydroxy-4-nitrobenzoate
- Ethyl pentanoate
- Ethyl crotonate
- Ethyl orthoformate
- Propyl succinate

Ketones

- Acetone
- 2-Butanone
- 3-Methyl-2-butanone
- 2-Pentanone
- 2-Butanone
- Cyclopentanone
- Acetylacetone
- Benzoylacetone
- 4-Methylcyclohexanone
- Cyclohexanone
- Benzophenone
- Acetophenone
- Fluorenone
- Benzoin
- Benzil
- Dibenzylacetone
- Anthrone
- 1,2-Cyclohexanedione
- 2,4-Hexanedione

Amides

- N,N-Dimethylformamide
- N,N-Diethylformamide
- Formanilide
- Acetamide
- Octanamide
- Dodecanamide
- Adipamide
- Benzanilide
- Benzamide
- Malonamide
- Urea
- Chloroacetamide
- Salicylamide
- Acetylsalicylamide
- Phthalimide
- Tetrahydrophthalimide
- *p*-Toluamide
- Dicyandiamide
- Glutaramide
- Benzylurea
- Stearamide
- Nicotinamide
- Succinimide
- Succinamide
- Acetanilide

Ethers

- Ethylmethyl ether
- Ethylene oxide
- Ethyl ether
- 1,3-Epoxypropane
- Butylmethyl ether
- Isopropyl ether
- Tetrahydrofuran
- 1,4-Dioxane
- Propyl ether
- 1,2-Dimethoxyethane
- 1,3-Dioxane
- Phenetole
- Anisole
- Ethylglycol
- Butylglycol
- Methylglycol
- 1-Naphthyl ether
- Trioxane
- Butoxyethanol
- 1-Butoxy-2-ethoxyethane
- 2-Ethoxyethanol

Polyalcohols

- Ethyleneglycol
- Diethyleneglycol
- Polyethyleneglycol 200
- Propyleneglycol
- Polyethyleneglycol 300
- Glycerin
- Methylethyleneglycol
- Methylglycol
- Polyglycol 1000
- Polyglycol 1500

Phenols

- Phenol
- *o*-Cresol
- *p*-Cresol
- *m*-Cresol
- 2-Ethylphenol
- *p*-Nitrophenol
- *o*-Nitrophenol
- 1-Naphthol
- 2-Naphthol
- 2,4-Dinitrophenol
- Hydroquinone
- Resorcinol
- 1,2-Dihydroxybenzene
- 8-Hydroxyquinoline
- Guaiacol
- Mercaptohydroquinone
- Thymol[a]
- Carvacrol

Quinones and nitro derivatives

- Nitromethane
- Nitrobenzene
- *o*-Nitrotoluene
- 2-Ethoxynitrobenzene
- *p*-Nitrotoluene
- *o*-Nitroaniline
- 1-Nitronaphthalene
- *m*-Dinitrobenzene
- 2,4,6-Trinitrophenol
- *p*-Quinone
- Anthraquinone
- 1,1-Napthoquinone

Heterocycles

- Furan[a]
- Tetrahydrofuran

Nitriles

- Acetonitrile
- Propionitrile
- Adiponitrile
- Succinonitrile
- Phenylsuccinonitrile
- *p*-Chlorophenylsuccinonitrile
- *p*-Methoxyphenylsuccinonitrile

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[a] Negative test.

ZUSAMMENFASSUNG

Ein neuer Mikro- oder Halbmikro-Nachweis von Sauerstoff in organischen Verbindungen beruht auf der blauen Farbe, die sich bei der Behandlung mit festem Kaliumthiocyanatocobaltat ergibt. Der Nachweis wurde mit etwa 500 Verbindungen, die verschiedene funktionelle Gruppen enthielten, geprüft; nur sehr wenige anomale Reaktionen wurden beobachtet.

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COMPLEXES OF ORGANOLEAD AND ORGANOTIN IONS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Numerous papers dealing with organic complexes of alkyl or aryl tin or lead cations have appeared in recent years, but there is very little information on the stability of these complexes. It has been established that alkyl tin and lead ions form stable coordination compounds with dithizone[1-3], 8-hydroxyquinoline[4-6], 2,2'-dipyridyl[4,6,7], phenanthroline[4,7,8], acetylacetone[8,9], picolinic acid[8], alizarin-S[10] and PAR[11]; however, only recently have the stability constants of dimethyltin with phenanthroline, acetylacetone and picolinic acid been determined[8].

In the present study the stability constants of complexes containing the ligand 1-(2-pyridylazo)-2-naphthol (PAN), have been determined for the dimethyl-, diethyl-, di-*n*-butyl- and diphenyltin and diethyllead ions in order to evaluate the analytical possibilities of this ligand for alkyltin and -lead ions. PAN has, of course, been widely used in recent years both as a metallochromic indicator and as a reagent for spectrophotometric determinations. Recently, the compositions of the respective chelates with Ni, Co, Zn, Cu and Mn were determined and the stability constants were calculated[12,13]. In studies of R_2Sn^{2+} solutions there is considerable uncertainty regarding the ionic species which may be present. Potentiometric investigations of dimethyltin(IV) hydrolysis have shown the existence of the $(CH_3)_2Sn^{2+}$ ion alone, up to a limiting pH of about 2[14-16].

In the present work, a preliminary study was made of the other ions in order to establish the pH values within which the ions that do not undergo hydrolytic equilibria, could be readily studied as to complex formation.

Since PAN is insoluble in water but sufficiently soluble in aqueous 20% (v/v) dioxane, this latter solvent was used. The constants were determined spectrophotometrically. In the case of the organolead compound for which hydrolytic equilibria can be ignored[17], the stability constant was also obtained by means of solvent extraction.

EXPERIMENTAL

Reagents

Diethyllead dichloride was prepared by the method of HEAP *et al.*[18]. Dimethyl-, diethyl- and di-*n*-butyltin dichlorides were prepared by the method of KOZESCHKOW[19]. Diphenyltin dichloride (Fluka A.G.) was purified by recrystallization. The melting points were used as a criterion of purity.

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* Ricercatore del C.N.R.

Dialkyltin perchlorate solutions were prepared by dissolving weighed amounts of R_2SnO in excess of standard perchloric acid. The dialkyltin content of the solutions was determined by amperometric titration with 8-hydroxyquinoline ($R=CH_3$, C_2H_5) or with potassium hexacyanoferrate(II) ($R=C_4H_8$, C_6H_5)[20]. The total perchlorate concentration of the stock solutions was determined by passing an aliquot of the solution through the cation-exchange resin Dowex 50W-X8 (H^+-form) and titrating the eluate with standard sodium hydroxide. Thus the free hydrogen ion concentration was known:

$$[H^+]=[ClO_4^-]-2\,[R_2Sn^{2+}] \tag{1}$$

The R_2SnO compounds were prepared from R_2SnCl_2. The dichlorides were dissolved in distilled water and the R_2SnO compounds were precipitated from the solution with dilute sodium hydroxide solution. The precipitate was washed with water until no chloride ion could be detected, and dried in a vacuum oven to constant weight.

PAN. PAN (C. Erba, Italy) was recrystallized from aqueous ethanol (m.p. 140–141°).

Dioxane. Commercial grade dioxane was boiled under reflux for 7 h with 10% of its volume of 1 *N* hydrochloric acid, a slow stream of air being passed in through the condenser. The distilled dioxane was treated with potassium hydroxide and the aqueous layer removed. The filtrate was distilled from potassium hydroxide pellets (b.p. 100–101°).

All the other chemicals employed were reagent grade, used without further purification.

Apparatus

Unicam spectrophotometer, Model SP 800; Zeiss spectrophotometer, Model PMQ II; Knick pH-meter, Model "pH 350".

RESULTS

Determination of the hydrolysis constants

The equilibrium hydrogen ion concentration in perchloric acid solutions of dialkyltin perchlorate was determined by the cell: $Hg|Hg_2Cl_2,\ KCl_{sat}||0.1\ M\ NaClO_4||B\ mM\ R_2Sn^{2+},\ H\ mM\ H^+,\ (100\text{-}2B\text{-}H)\ mM\ Na^+,\ 0.1\ M\ ClO_4^-|$glass electrode. The glass electrode was tested in the pH range 1–4 for the titration of perchloric acid with sodium hydroxide. The e.m.f. in mV was described by the equation:

$$E_g=E^0+59.16\log H^+\ mM\ -0.225\ H^+\ mM \tag{2}$$

Cell potentials were read at 0.1 mV using a Leeds–Northrup K-3 potentiometer with a Cary 31-V vibrating reed electrometer as the null-point indicator. The temperature was thermostatically controlled at 25±0.1°. With B equal to the total R_2Sn^{2+} concentration, b the equilibrium concentration of R_2Sn^{2+}, H the analytical $[H^+]$, assuming no hydrolysis, and $h=[H^+]$, for the titration of acidic solutions of dialkyltin perchlorate with sodium hydroxide, it was possible to construct the curves n_{OH} *vs.* $-\log[H^+]_B$, where n_{OH} (average number of OH^- bound to the central atom) was obtained from the equation:

$$n_{\mathrm{OH}} = h - H - K_{\mathrm{w}}h^{-1}/B \qquad (3)$$

In Fig. 1 the curves related to the diethyltin ion are reported. By comparing the experimental log B *vs.* $(-\log h)_n$ data with normalized curves, it was possible to calculate by SILLEN's method[21,22] the hydrolysis constants β_{11} and β_{22}, for the $(CH_3)_2Sn^{2+}$ and $(C_2H_5)_2Sn^{2+}$ compounds for the reactions:

$$R_2Sn^{2+} + H_2O \rightleftarrows R_2SnOH^+ + H^+ \qquad (4)$$

$$2\ R_2Sn^{2+} + 2\ H_2O \leftrightarrows (R_2SnOH)_2{}^{2+} + 2\ H^+ \qquad (5)$$

In the case of $(C_4H_9)_2Sn^{2+}$ it was sufficient, at least for this study, to ascertain that hydrolysis up to a pH of 2 was not relevant, having established that at this value n_{OH} corresponds to about 0.15. On the other hand, a more complete study of the hydrolytic equilibria would have been complicated by the fact that even at pH 2.3 precipitation occurs. In the case of $(C_6H_5)_2Sn^{2+}$, which likewise precipitates at approximately pH 2, the first constant was nevertheless determined, although only

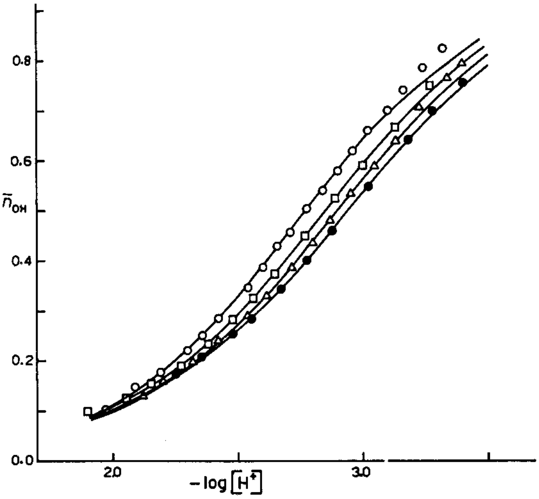

Fig. 1. Average number of OH^- bound per diethyltin ion as a function of $-\log[H^+]$. B = ○ 44.87 mM, □ 21.13 mM, △ 10.57 mM, ● 3.03 mM. Curves calculated for log $\beta_{11} = -2.96$, log $\beta_{22} = -4.66$.

TABLE I

HYDROLYSIS CONSTANTS OF R_2Sn^{2+} COMPOUNDS

Species	*log β_{11}*	*log β_{22}*	*Medium*	*References*
$(CH_3)_2Sn^{2+}$	-3.12	-4.60	0.1 M ClO_4^-	This work
	-3.45	-4.74	3 M ClO_4^-	14
	-3.18	-4.66	0.1 M NO_3^-	9
	-3.25	-5.05	0.1 M Cl^-	15
$(C_2H_5)_2Sn^{2+}$	-2.96	-4.66	0.1 M ClO_4^-	This work
$(C_6H_5)_2Sn^{2+}$	-2.0 ± 0.2		0.1 M ClO_4^-	This work

approximately, since hydrolysis started at pH *ca.* 1.5. The constants so obtained are reported in Table I.

Spectrophotometric studies

When a dialkyl tin or lead ion is added to a solution of PAN, the yellow ligand becomes the red chelate. The colour occurs upon mixing, and its intensity remains constant for at least 24 h. From the spectra of solutions containing a large excess of the organometallic ion, the maximum wavelengths and the corresponding molar extinction coefficients were obtained (Table II). JOB's plots[23,24] provided further evidence of the 1:1 cation–ligand ratio for all the compounds examined. In Fig. 2a and 2b two typical examples are reported. For the organolead cation, which is much less acidic than the organotin compounds, it was possible to verify the above ratio by direct spectrophotometric titration with standard PAN solution. It follows that the complex reaction can be represented by:

TABLE II

ABSORPTION DATA OF PAN CHELATES IN AQUEOUS 20% DIOXANE

Compound	*λ max*	*ε · 10⁻³*
$(CH_3)_2Sn^{2+}$	532	21.1
$(C_2H_5)_2Sn^{2+}$	538	22.6
$(C_4H_9)_2Sn^{2+}$	540	22.5
$(C_6H_5)_2Sn^{2+}$	542	22.0
$(C_2H_5)_2Pb^{2+}$	540	22.3

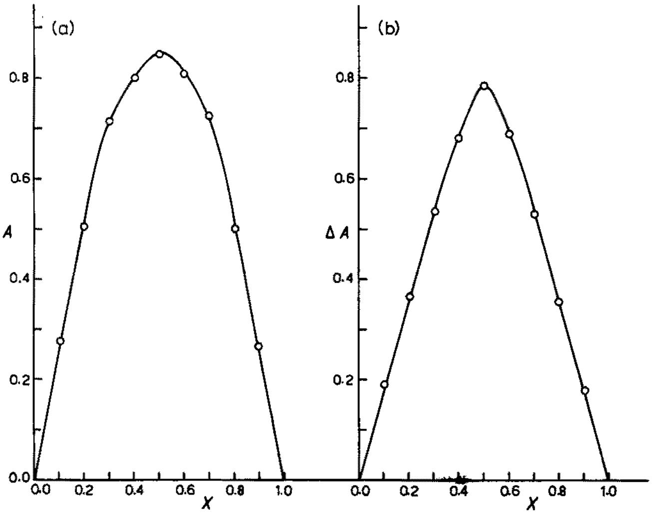

Fig. 2a. Corrected continuous variation curve for diethyltin–PAN chelate (pH 2.0, 538 nm, $[PAN] + [(C_2H_5)_2Sn^{2+}] = 4.0 \cdot 10^{-4}$ *M*, $X = [(C_2H_5)_2Sn^{2+}]/[(C_2H_5)_2Sn^{2+}] + [PAN]$.

Fig. 2b. Corrected continuous variation curve for diethyllead–PAN chelate (pH 8.2, 540 nm, $[PAN] + [(C_2H_5)_2Pb^{2+}] = 8.0 \cdot 10^{-5}$ *M*, $X = [(C_2H_5)_2Pb^{2+}]/[(C_2H_5)_2Pb^{2+}] + [PAN]$.

$$R_2M^{2+} + HL^{+} \leftrightarrows R_2ML^{+} + H^{+} \qquad (6)$$

(M = Sn, Pb). In order to calculate the constants K for the reaction (6), known amounts of the organometallic ion, of standard PAN solution in dioxane and of standard perchloric acid were introduced into 25-ml volumetric flasks, and the solutions were diluted with sodium perchlorate solution and dioxane so that 20% (v/v) dioxane would be present and the ionic strength would be equal to 0.1 M ClO_4^-.

If it is assumed that hydrolyzed species are absent, the following equations apply:

$$[R_2M^{2+}]_t = [R_2M^{2+}] + [R_2ML^+] \qquad (7)$$

and since $K_{a2} = [H^+]\,[L^-]/[HL] = 6 \cdot 10^{-13}$ and the experiments were carried out at pH values < 5

$$[PAN]_t = [R_2ML^+] + [HL] + [H_2L^+] \qquad (8)$$

The concentration of the complex was determined by measuring the total absorbance of the solutions at the wavelength of maximum absorption of the chelates. In order to correct their total absorbance (A_t) for the contribution, even though negligible, of the unbound ligand ($HL + H_2L^+$), its apparent molar extinction coefficient at the wavelength of maximum absorption of the chelates and at the various pre-chosen pH values ($\varepsilon_{HL+H_2L^+}$) was determined photometrically using the same series of solutions as above, but without the organometallic ion.

Combining the expression for total absorption

$$A_t = \varepsilon_{R_2ML^+}[R_2ML^+] + \varepsilon_{(HL+H_2L^+)}\,\{[HL] + [H_2L^+]\} \qquad (9)$$

with eqn. (8), the complex concentrations and the sum of the $[HL] + [H_2L^+]$ terms

TABLE III

COMPLEX FORMATION OF PAN WITH THE DI-n-BUTYLTIN(IV) ION

($[(C_4H_9)_2Sn^{2+}]_t = 4.0 \cdot 10^{-4}\ M$; $[PAN]_t = 2.0 \cdot 10^{-4}\ M$)

$[H^+] \cdot 10^2$	A_t	$\varepsilon_{(HL+H_2L^+)}$	$[(C_4H_9)_2SnL^+] \cdot 10^5$	$[HL]+[H_2L^+] \cdot 10^4$	$[HL] \cdot 10^5$	$[(C_4H_9)_2Sn^{2+}] \cdot 10^4$	K
12.59	0.117	210	0.336	1.966	0.751	3.966	142
10.12	0.161	215	0.530	1.947	0.917	3.947	148
8.81	0.190	225	0.651	1.935	1.039	3.935	140
7.85	0.236	225	0.857	1.914	1.146	3.914	150
6.76	0.292	225	1.109	1.889	1.301	3.889	148
5.62	0.377	230	1.486	1.851	1.512	3.851	143
4.78	0.478	235	1.935	1.806	1.710	3.806	142
4.36	0.554	240	2.273	1.772	1.823	3.772	144
4.07	0.608	240	2.516	1.748	1.912	3.748	143
3.67	0.696	245	2.907	1.709	2.049	3.709	140
3.46	0.753	245	3.163	1.684	2.125	3.684	140
3.16	0.425[a]	250	3.595	1.640	2.240	3.640	139
2.91	0.471[a]	250	4.010	1.599	2.344	3.599	138
2.48	0.576[a]	250	4.953	1.505	2.524	3.505	138
2.08	0.696[a]	255	6.028	1.397	2.708	3.397	136
1.67	0.174[b]	260	7.590	1.242	2.862	3.242	136
1.05	0.251[b]	275	11.046	0.895	2.887	2.895	139
							Average value 142 ± 6

[a] 0.5-cm cuvettes.
[b] 0.1-cm cuvettes.

were obtained. Since the first dissociation constant of the ligand

$$K_{a1} = [HL]\,[H^+]/[H_2L^+] \tag{10}$$

and the $[H^+]$ measured potentiometrically with a glass electrode standardized in 20% dioxane were known, it was possible to determine the K values by means of eqns. (7) and (10). The results from a typical run are given in Table III. When K was divided by K_{a2}, the K_f values for the following equilibrium were obtained as reported in Table IV:

$$R_2M^{2+} + L^- \rightleftharpoons R_2ML^+ \tag{11}$$

While the literature value[25] of $6 \cdot 10^{-13}$ was used for K_{a2}, the value of $5 \cdot 10^{-3}$ which we found in 20% dioxane at a 0.1 M perchlorate concentration was used for K_{a1}.

TABLE IV

CHELATE FORMATION CONSTANTS OF PAN DETERMINED SPECTROPHOTOMETRICALLY AT 25° IN AQUEOUS 20 % (v/v) DIOXANE

Compound	*No. of protons released on complex formation*	*Ion : PAN ratio in complex*	*K*	*log K_f*	*log K_H*
$(CH_3)_2Sn^{2+}$	1	1:1	2.11	12.55	—
$(C_2H_5)_2Sn^{2+}$	1	1:1	32.0	13.73	—
$(C_4H_9)_2Sn^{2+}$	1	1:1	142	14.37	—
$(C_6H_5)_2Sn^{2+}$	1	1:1	290	14.68	—
$(C_2H_5)_2Pb^{2+}$	1	1:1	0.72	12.08	—
	2[a]	1:1[a]		≥12[a]	−6.8[a]

[a] Values determined by solvent extraction.

As mentioned above, the studies were limited to pH values for which the presence of only the single species R_2Sn^{2+} was certain, and the formation of competitive complexes, in particular those of mixed hydroxo complexes, was excluded. In fact, even if the presence of the ligand should reduce the tendency towards formation of hydroxo complexes, the possibility that water coordinated to the charged complex R_2SnL^+ could still transfer protons in less acidic solutions was not excluded.

Experiments carried out on the single cations $(CH_3)_2Sn^{2+}$ and $(C_2H_5)_2Sn^{2+}$ for which the hydrolysis constants were accurately calculated, showed that the data obtained spectrophotometrically at pH values where cation hydrolysis had already occurred to appreciable extents, could not be interpreted on the basis of formation of the single chelate R_2SnL^+, arising from the single species R_2Sn^{2+}, alone. In fact, when the concentration of the free organometallic ion in eqn. (7) was calculated on the basis of hydrolysis constants, the K values for the reaction steadily increased. This can be explained if it is assumed either that the species R_2SnOH^+ is susceptible to chelation or that the following hydrolysis reaction takes place:

$$R_2SnL^+ + H_2O \leftrightharpoons R_2SnL(OH) + H^+ \tag{12}$$

In both cases the neutral complex $R_2SnL(OH)$ would be formed and would not be spectrophotometrically distinguishable from the charged complex. It is worth noting that the chelates R_2Sn–PAN can be readily extracted by chloroform, and that the visible spectra of the extracted chelates are more or less similar to that obtained in aqueous solution, both in regard to spectral arrangement as well as molar extinction coefficient.

Paper electrophoretic measurements on the ligand showed that, even though the chelate migrates to the cathode at pH 2, there is no migration at pH 4.5, indicating precipitation or a neutral species. At any rate, for tin it is not possible to exclude the presence of more complex neutral species; even if only the single species, $R_2SnL(OH)$, is present, it is not possible to decide its exact mode of formation. For lead, as long as there is no hydrolysis of the cation, the only probable reaction is that of eqn. (12). For this reaction the formation of the chelate was studied by solvent extraction; the data obtained were not only in agreement with those obtained spectrophotometrically, but also allowed the calculation of the equilibrium constant.

Determination of the distribution equilibria

A series of extractions was carried out over a range of $(C_2H_5)_2Pb^{2+}$ concentrations and pH values. A known volume (25 ml) of aqueous solution, made up of solutions of $(C_2H_5)_2PbCl_2$, $NaClO_4$, $HClO_4$, and NaOH so to maintain a constant ionic strength (0.1 *M* ClO_4^-) and a pH close to a previously established value, was transferred to a polyethylene container; an equal volume of PAN in chloroform was added, and the resulting solution was shaken for 5 h. After equilibration the solution was centrifuged, the two phases were separated and aliquots were taken from both.

The $(C_2H_5)_2Pb^{2+}$ was determined photometrically by measuring the absorbance of the organic layer at 555 nm (corresponding to the maximum of the uncharged complex) and, if necessary, by analyzing the aqueous phase with PAR[11]. For the calibration curve aqueous solutions of known $(C_2H_5)_2Pb^{2+}$ concentration in a borate–perchloric acid buffer of pH 8.2, were repeatedly extracted with chloroform solutions of 10^{-2} *M* PAN. For the blank, PAN in chloroform was used to extract solutions containing $HClO_4$, $NaClO_4$ and NaOH alone; buffers were not used in order to avoid the formation of auxiliary complexes. The proton concentration was determined by measuring the pH of the aqueous phase using a glass electrode. Experimental values obtained in the distribution studies are reported in Table V.

If chelation takes place in the aqueous phase and a neutral extractable species is formed, then, in the absence of side reactions, the distribution ratio, *D*, of the ion is given by:

$$D = K_f \cdot K_{DX} \cdot K_{a2}^n \, [HL]_0^n / K_{DL}^n \cdot [H^+]^n \qquad (13)$$

In this expression K_f represents the stability constant of the complex, K_{DX} the distribution ratio of the complex, K_{DL} the distribution ratio of the reagent, K_{a2} the acidic dissociation constant of the ligand, and n the number of ligand molecules bound per mole of cation.

From the slopes of the curves log *D* *vs.* pH and log *D* *vs.* log HL_0 (Figs. 3 and 4), n has a value of 1, which indicates the formation of a 1:1 PAN: $(C_2H_5)_2Pb^{2+}$ complex. Since the results are the same both when NaCl and HCl are used instead of $NaClO_4$ and $HClO_4$, and when the concentrations of these electrolytes are varied, we propose, as for the copper (II) extraction[13], the following scheme of reactions:

$$HL_0 \leftrightarrows HL_w \qquad (14)$$

TABLE V

EXTRACTION OF $(C_2H_5)_2Pb^{2+}$ INTO $CHCl_3$ WITH $1 \cdot 10^{-3}$ *M* PAN

pH	*$[(C_2H_5)_2Pb^{2+}]_t \cdot 10^5$*	*$[(C_2H_5)_2Pb^{2+}]_0 \cdot 10^5$*	*$[(C_2H_5)_2Pb^{2+}]_w \cdot 10^5$*	*log D*
2.52	8.00	0.024	7.976	−2.52
2.99	2.40	0.033	2.367	−1.86
3.02	8.00	0.104	7.896	−1.88
3.39	2.40	0.076	2.324	−1.48
3.37	4.00	0.152	3.848	−1.40
3.365	8.00	0.288	7.712	−1.43
3.99	8.00	0.868	7.132	−0.91
4.03	2.40	0.259	2.141	−0.91
4.05	4.00	0.466	3.534	−0.88
4.55	4.00	1.315	2.685	−0.31
4.61	8.00	2.188	5.812	−0.42
4.68	2.40	0.729	1.671	−0.36
5.15	8.00	4.400	3.600	+0.09
5.24	4.00	2.272	1.728	0.12
5.08	2.40	1.498	0.902	0.22
5.80	2.40	1.800	0.600	0.47
5.79	4.00	2.876	1.124	0.41
5.70	8.00	6.400	1.600	0.60
6.00	4.00	3.632	0.368	0.99
6.11	2.40	2.172	0.228	0.99
6.12	4.00	3.782	0.218	1.24
6.27	2.40	2.288	0.112	1.30
6.64	4.00	3.960	0.040	1.99
7.70	4.00	3.760	0.240	1.70
7.76	4.00	3.960	0.040	2.12
8.13	2.40	2.376	0.024	1.99
8.325	4.00	3.920	0.080	1.69
8.373	4.00	3.880	0.120	1.83
8.64	4.00	3.860	0.140	1.97
8.58	2.40	2.384	0.016	2.17
8.76	4.00	3.920	0.080	1.69
9.07	2.40	2.332	0.068	1.92
9.09	4.00	3.920	0.080	1.69
9.63	2.40	2.260	0.140	1.21
9.655	4.00	3.708	0.292	1.10
9.785	4.00	2.815	1.185	0.38
9.77	2.40	1.896	0.504	0.57
9.765	4.00	3.060	0.940	0.51
10.465	2.40	1.032	1.368	−0.12
10.45	4.00	1.712	2.288	−0.13

$$HL_w \leftrightarrows H^+ + L^- \tag{15}$$

$$(C_2H_5)_2Pb^{2+} + L^- \leftrightarrows (C_2H_5)_2PbL^+ \tag{16}$$

$$(C_2H_5)_2PbL^+ + H_2O \leftrightarrows (C_2H_5)_2PbL(OH) + H^+ \tag{17}$$

$$(C_2H_5)_2PbL(OH)_w \leftrightarrows (C_2H_5)_2PbL(OH)_0 \tag{18}$$

With

$$K_H = [H^+]\,[(C_2H_5)_2PbL(OH)]/[(C_2H_5)_2PbL^+] \tag{19}$$

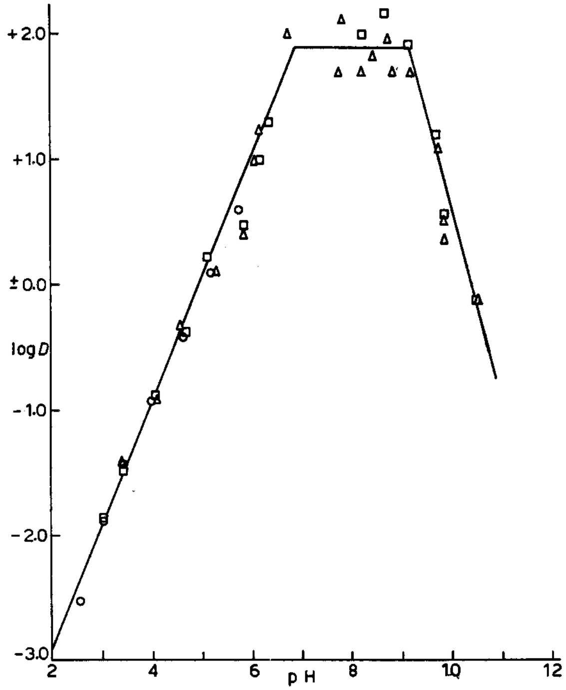

Fig. 3. Effect of pH on extraction of diethyllead chelate of PAN. $[(C_2H_5)_2Pb^{2+}]_t$ = ○ $8.0 \cdot 10^{-5}$ *M*, △ $4.0 \cdot 10^{-5}$ *M*, □ $2.4 \cdot 10^{-5}$ *M*.

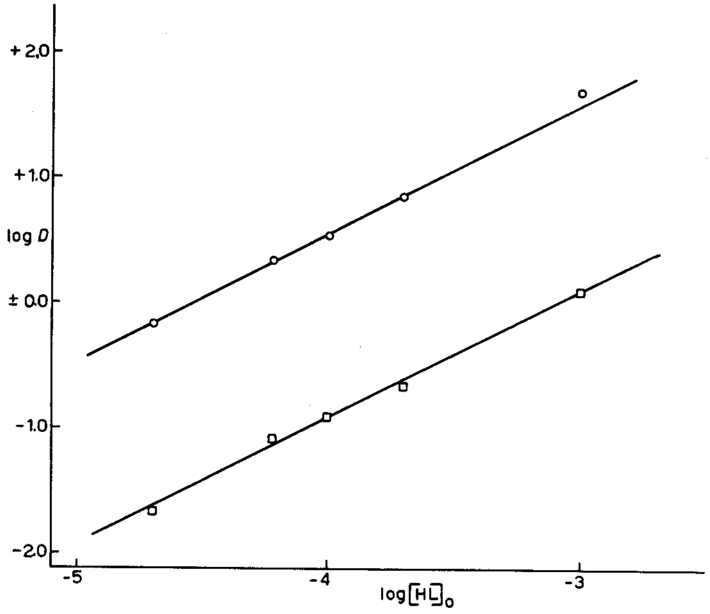

Fig. 4. Effect of PAN concentration on extraction of diethyllead chelate. $[(C_2H_5)_2Pb^{2+}]$ = $2.4 \cdot 10^{-5}$ *M*, pH = ○ 8.15, □ 5.20.

and with

$$K'_{DX} = [(C_2H_5)_2PbL(OH)]_0/[(C_2H_5)_2PbL(OH)]_w \qquad (20)$$

eqn. (13) becomes

$$D = \frac{K'_{DX}\,K_H}{\dfrac{[H^+]^2 \cdot K_{DL}}{K_f \cdot K_{a2}\,[HL]_0} + H^+ + K_H} \qquad (21)$$

If K_f is very large, a slope of 1 is observed with pH variation, since the expression reduces to:

$$D = \frac{K'_{DX} \cdot K_H}{[H^+] + K_H} \text{ or } \qquad D = \frac{K'_{DX} \cdot K_H}{[H^+]} \qquad (22)$$

When these equations were used and the values of 1.9, 5.4 and 11.2 were inserted for log K'_{DX}, log K_{DL} and pK_{a2} respectively[13], log K_H was found to be -6.8 and log $K_f \geqslant 12$, in close agreement with the spectrophotometric value.

DISCUSSION

The stability constants reported in Table IV show that tin coordinates more readily than lead and that, in the series studied, the stability of the tin complexes decreases in the order Ph > But > Et > Me. This sequence can be justified on the basis of an increase in the electrophilic strength of the tin with an increase in the length of the R-groups attached to tin. The particularly high stability of the phenyl derivative may be explained by inductive effects and by a delocalization of the positive charge of the complex due to mesomeric effects.

The high stability of these chelates agrees well with the established action of PAN as a tridentate ligand[12,13,26], chelate systems with five-membered rings being formed. Both tin and lead could assume a coordination number of 5 in the charged complex and a coordination number of 6 in the extractable neutral complex; this is so if one does not assume that a solvent molecule remains coordinated in the charged complex, so that, in effect, only a six-coordinated central atom would exist. Both the possible structures have been verified by other authors.

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SUMMARY

The stability constants of the complexes of 1-(2-pyridylazo)-2-naphthol with several organotin and lead ions were determined spectrophotometrically in aqueous 20% (v/v) dioxane and were shown to have very high values. The extraction of the complex of $(C_2H_5)_2Pb^{2+}$ from water into chloroform was studied, and the formation of an extractable $(C_2H_5)_2Pb(PAN)(OH)$ complex is postulated.

RÉSUMÉ

On a effectué une détermination spectrophotométrique des constantes de stabilité des complexes entre le 1-(2-pyridylazo)-2-naphtol et plusieurs ions organométalliques de l'étain et du plomb. Les valeurs de ces constantes sont très élevées. Pour le cation $(C_2H_5)_2Pb^{2+}$, on a étudié également l'extraction de son complexe dans le chloroforme. On peut admettre qu'il y a formation du complexe $(C_2H_5)_2Pb(PAN)(OH)$.

ZUSAMMENFASSUNG

Die Stabilitätskonstanten der Komplexe von Dialkylblei und Zinnionen mit 1-(2-Pyridylazo)-2-Naphthol in einem Gemisch aus Wasser und 20% Dioxan wurden spektralphotometrisch bestimmt. Die Extraktion des $(C_2H_5)_2Pb^+$-Komplexes aus Wasser mit Chloroform wurde untersucht. Die Bildung eines extrahierbaren $(C_2H_5)_2Pb(PAN)(OH)$-Komplexes wird angenommen.

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SIMULTANEOUS DETERMINATION OF FLUORINE AND CHLORINE IN SILICATE ROCKS BY A RAPID SPECTROPHOTOMETRIC METHOD

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Interest in the geochemistry of fluorine and chlorine has established a need for a rapid and accurate method for the determination of these elements in silicate rocks[1,2]. The conventional determination of fluorine in rocks involves isolation of fluorine by some modification[3-6] of the WILLARD AND WINTER distillation method[8], followed either by titration with standard thorium nitrate[4] or by colorimetric determination with a thorium–SPADNS[5,9] or with a zirconium–SPADNS reagent[6,7]. The presence of some ions prevents quantitative distillation[10-12] or causes interference in the colorimetric measurement. These methods moreover lack rapidity and/or accuracy when applied directly to silicate rock samples. GLASÖ[12] preferred an ion-exchange method to remove fluoride from interfering substances for analysis of iron ores. The disadvantage of this method is that it is too time-consuming and is susceptible to serious errors due to incomplete separation of fluoride.

Many methods have been published for the determination of chlorine in rocks, but most of them are not applicable to the rapid, precise determination of microgram amounts of chlorine in silicate rocks of wide range of chemical composition. The classical silver chloride precipitation method[3] is time-consuming if a large number of analyses must be made. The photometric sulfide method[13] and its modifications[14,15] was investigated initially for the determination of chlorine in some geochemical standards. The procedure is time-consuming and required considerable chemical manipulation, thereby increasing the possibility of contamination and leading to less than desirable accuracy. PECK AND TOMASI's[16] titration method is not accurate enough for determination of microgram amounts of chlorine, particularly in the ultramafic rocks. The accuracy of the micro diffusion–titration procedure[17,18] is not sufficient, particularly below 50 μg because the amount of chloride approaches the sensitivity limits of the procedure[19].

A rapid spectrophotometric method has been developed for simultaneous determination of fluorine and chlorine. The method involves taking separate aliquots of a single sample dissolution. Fluorine, without separation, was determined utilizing zirconium–eriochrome cyanine R after a modification of the method by MEGREGIAN[20] and SARMA[21], whereas chlorine was determined utilizing the stable colored iron(III) thiocyanate complex following a modification of the method of BERGMANN AND SANIK[19] and ROWE[22]. This method gives greater speed, sensitivity and precision, and presumably greater accuracy, because of less probable contamination during the simpler chemical treatment involved.

EXPERIMENTAL

Apparatus

A Beckman Model DU-2 Spectrophotometer was used in conjunction with matched 1.0-cm silica cells for all absorbance measurements.

Fisher vacuum Filtrator and Whatman No. 5 filter paper.

Electric muffle furnace for continuous operation at 900°.

All glassware is cleaned with nitric acid, rinsed with distilled water and finally with double-distilled water.

Reagents and solutions

Double-distilled water is used for reagent preparation and throughout the procedure.

Eriochrome cyanine R (or alizarol cyanine R C—Fisher) (reagent A for F). Dissolve 1.800 g in 1 l of water.

Zirconyl chloride (reagent B for F). Dissolve 0.265 g of $ZrOCl_2 \cdot 8H_2O$ (Fisher) in about 10 ml of water and dilute with concentrated hydrochloric acid to 1 l.

Ferric ammonium sulfate solution (reagent A for Cl). Dissolve 12.055 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ (Fisher) in 100 ml of 9 *M* nitric acid.

Saturated mercury(II) thiocyanate (reagent B for Cl). Dissolve 0.35 g of $Hg(SCN)_2$ (Fisher) in 100 ml of 95% ethanol and allow to stand overnight to precipitate excess sol before use.

Standard sodium fluoride solution (5 µg/ml). Dry reagent-grade (Fisher) NaF for 2 h at 110° and cool in a desiccator. Dissolve 0.5525 g in 1 l of water, take a 5-ml aliquot and dilute to 250 ml. Store in a polyethylene bottle. A solution (5 µg/ml) so prepared was checked by the lead chlorofluoride method, and appropriate correction was made.

Standard sodium chloride solution (10 µg/ml). Dry reagent-grade NaCl (Fisher) for 2 h at 110° and cool in a desiccator. Dissolve 0.8242 g in 500 ml of water, take a 5-ml aliquot and dilute to 500 ml. The latter solution contains 10 µg of sodium chloride per ml.

Reference solution (for F). 10 ml of reagent A (for F) were added to 100 ml of water and 10 ml of concentrated hydrochloric acid. This solution is used for setting the zero point (absorbance) of spectrophotometer.

Procedure

Decomposition and isolation. Dry a powdered sample of rock at 110° for 1 h and cool in a desiccator. Mix 0.500 g of powder (90 mesh) with a flux mixture of 3.500 g of sodium carbonate and 0.600 g of zinc oxide in a 50-ml platinum crucible, and fuse in an electric muffle furnace at 900° for 20–25 min.

Cool the crucible, and add 10 ml of water and 3 drops of ethanol (95%) to reduce any manganate present. Place the crucible and contents on a hot plate, boil for 1 min, and let the solution stand to dissolve the soluble material.

Filter the solution through a washed filter paper (Whatman No. 5) into a 100-ml polyethylene beaker by means of vacuum Filtrator. Crush the cake with a flat-ended rod and stir the solution before each portion is pipetted to the filter. Wash the residue 5 times by decantation with 2 ml of hot water and discard the residue.

Cover the beaker, add cautiously 4.1 ml of concentrated nitric acid through the lip of the beaker to neutralize the solution (slightly acidic), and stir the solution to expel most of the CO_2. Wash the cover glass, rod, and the inside of the beaker with water, and transfer the solution into a 50-ml flask and make up to volume. Pipette separate aliquots of this solution for the determinations of fluorine and chlorine.

In parallel with each batch of analyses, run a blank by taking 3.500 g of sodium carbonate and 0.600 g of zinc oxide, and treating as described above.

Fluorine determination. Pipette a 5.0-ml aliquot of the sample solution into a 50-ml flask, add 3 drops of 6 N sodium hydroxide and mix well. Then add 3.0 ml of reagent A and 5.0 ml of reagent B, dilute with water to the mark and shake well. This solution should not contain more than 80 μg of fluorine.

Allow the solution to stand for 1–1.5 h for elimination of aluminum interference[20], maintaining the temperature within $25 \pm 1°$. Measure the absorbances of both sample and blank at 532 mμ against a reference solution, and obtain the fluorine content from the difference between the two absorbances by reference to a standard curve.

Prepare the standard curve by taking 0.0, 4.0, 8.0, 12.0, and 16.0 ml of standard sodium fluoride solution (5 μg F/ml). To each standard add 3 drops of 6 N sodium hydroxide, and reagent A and B as above, and follow the entire procedure as described above. Check the standard curve with each new batch of reagent A and B.

Chlorine determination. Pipette a 10-ml or 20-ml aliquot (depending on chlorine content in the sample) of the same sample solution into a 25-ml flask. Add 2.0 ml of reagent A and 2.0 ml of reagent B. Mix the solution, dilute to volume with water and mix again. Treat the blank in the same manner. Allow the color to develop for 10 min and measure the absorbances of the sample and blank against water in a 10-mm cell at 460 nm. Because any chloride present in the air is slowly absorbed, water is used in the reference cell instead of the blank. It is important that this measurement be completed within 30 min after mixing. Calculate the chlorine concentration corresponding to the difference between the two absorbances from a standard curve.

Prepare the standard curve by taking 0.0, 2.0, 4.0, 8.0, and 10.0 ml of a standard sodium chloride solution (10 μg/ml). Dilution, color development, and absorbance measurement are as outlined above. The variation in sensitivity resulting from the use of different batches of reagent A and B makes it necessary to check the standard curve for each set of determinations.

RESULTS AND DISCUSSION

Investigation and elimination of interferences

Fluorine. The interference of aluminum, iron(III), phosphate, and sulfate ions on the bleaching by fluoride of the zirconium–eriochrome cyanine R complex has been noted[20]. The use of sodium carbonate–zinc oxide flux mixture results in retention in the residue of phosphate and most of the cations common in silicates[23]. In particular iron and phosphate interference is eliminated at this point from the solutions which are subsequently analyzed. Most of the aluminum is also removed at this time. The alkaline filtrate never contains more than 25 mg of aluminum in most silicate rocks[4,6]. GLASÖ[12] observed that increasing the acidity can reduce the interference of aluminum, whereas MEGREGIAN[20] proposed treating with sodium hydroxide. Both processes were examined.

In order to understand fully the effect of interference of aluminum, known amounts of aluminum ion were added to solutions containing 20 μg of fluorine in 50 ml. Table I (Procedure I) shows that 1 mg Al per 50 ml of sample has no effect after 2 h. However, quantities up to 8 mg Al/50 ml of sample, presumably the maximum content present in the solution (50 ml), can be tolerated by adding 3 drops of 6 *N* sodium hydroxide to make the solution alkaline and then adding the reagents as in the regular procedure, provided that the solution is allowed to stand for 1–1.5 h before measuring (Procedure II). Sulfates react similarly to fluoride, but the sulfate content of most silicate rocks is below the level which would give rise to interference.

The effects of nickel(II) and chromium(III) were studied analogously, since these ions are present in substantial amounts in ultramafic rocks. No significant effect of these ions is indicated as shown in Table I.

TABLE I

EFFECT OF CERTAIN IONS ON FLUORINE DETERMINATION

Ion	*Amount added (μg)*	*F^- taken (μg)*	*F^- found (μg)*							
			Procedure I. Measured after:				*Procedure II. Measured after:*			
			¼ h	*½ h*	*1 h*	*2 h*	*¼ h*	*½ h*	*1 h*	*2 h*
Al^{3+}	500	20	0	12.5	19	20	3.0	15	20	20
	1000	20	0	9	17	19.5	0	12.5	20	20
	5000	20	0	4.5	15.5	19	0	8	19	20
	8000	20	0	2	14.5	17.5	0	5	18.5	19.5
Ni^{2+}	80	20	20.5	—	20	—	20.5	—	20	—
	320	20	21.0	—	20.5	—	20.5	—	20	—
Cr^{3+}	80	20	21.0	—	20	—	20.5	—	20	—
	260	20	20.5	—	20.5	—	20	—	20	—

TABLE II

EFFECT OF CERTAIN IONS ON CHLORINE DETERMINATION

Ion	*Amount added (μg)*	*Cl^- (μg)*		*% Error*
		Taken	*Found*	
F^-	50	20.7	20.7	—
	125	20.7	20.7	—
	250	20.7	20.5	−1.0
Ni^{2+}	40	20.7	20.7	—
	80	20.7	20.7	—
	160	20.7	20.6	+0.5
	320	20.7	21.4	+3.4
Cr^{3+}	40	20.7	20.7	—
	80	20.7	20.7	—
	160	20.7	21.3	+2.9
	260	20.7	21.6	+4.3

Chlorine. Interferences of a number of cations and anions were studied. The anions, nitrite, sulfide, cyanide and thiocyanate, can cause interference, but these ions are not present in quantity in most silicates. Bromine and iodine interfere but it is unlikely that either will be present in silicate rocks in more than trace amounts (usually less than 1 p.p.m. of Br and I in silicates).

The possible effect of fluoride interference was examined by adding known amounts of fluorine to a solution containing 20.7 μg Cl/25 ml. The data in Table II suggest that there is no significant interference of fluoride up to 250 μg/25 ml sample. Interference of nickel(II) and chromium(III) was tested; these ions color the solution and interfere if present in amounts greater than 100 μg/25 ml. However, since these ions are apparently not present in the alkaline filtrate, no further treatment is necessary.

Recovery of known fluorine and chlorine

A set of experiments was made to test the recovery of fluorine and chlorine from rocks. Known amounts of standard sodium fluoride solution and sodium chloride solution were added to 0.500-g standard rock samples (S-1, European standard shale; W-1, diabase standard). After careful evaporation with an infrared lamp, the samples were carried through the entire analytical procedure. The results are given in Table III and show the relative errors of the determinations to be less than 2.5%.

Reproducibility

The reproducibility of the method was tested by taking 0.500 g of European standard shale (S-1, high F and low Cl content) and diabase (W-1, low F and high Cl content) and following the procedure described above. The results (Table IV) demonstrate the reliability of the method. Each result represents a separately weighed sample taken through the entire procedure.

TABLE III

RECOVERY OF FLUORINE AND CHLORINE FROM STANDARD SILICATE ROCKS

Sample	*Fluorine*			*Chlorine*		
	Added (μg)	*Found (μg)*	*% Error*	*Added (μg)*	*Found (μg)*	*% Error*
S-1[a]	0 (Blank)	435	—	0 (Blank)	36.8	—
	125	554	1.1	30	65.1	2.5
	250	680	0.8	60	95.1	1.8
W-1[b]	0 (Blank)	105	—	0 (Blank)	92.5	—
	125	225	2.2	30	120.7	1.4
	250	350	1.4	60	150.5	1.3

[a] S-1 European standard shale.
[b] W-1 Diabase standard

TABLE IV

REPRODUCIBILITY OF THE RAPID METHOD

Sample	*Name*	*F*		*Cl*	
		p.p.m.	*Std. deviation*	*p.p.m.*	*Std. deviation*
S-1	European std. shale	885, 900 880, 870	9.11	70, 74 74, 71	2.1
W-1	Std. diabase	205, 210 210, 210	2.65	184, 190 188, 185	2.76

TABLE V

COMPARISON OF F AND Cl CONTENTS OF SOME GEOCHEMICAL STANDARDS BY DIFFERENT METHODS

Sample no.	*Name*	*p.p.m. F*		*p.p.m. Cl*	
		Others	*This work*[a]	*Others*	*This work*[a]
NBS 4999	NBS std. dunite	—	48	140[b]	106
S-1	European std. shale	760[e]	884	100[c]	72
GR	French std. granite	800[d] 1000[f]	925	400[d]	315
T-1	Tonalite std. (Tanganyika Geol. Survey)	400[d] 450[d] 400[f]	390	—	128
Syenite-1	C.A.A.S. std. (Canada)	1750[f]	1770	—	220

[a] Mean of 2 or more values. [b] HOERING AND PARKER (1961), one value. [c] WEDEPHOL (1966), one value. [d] THOMAS AND KEMPE[25], one value. [e] KORITNIG[26], mean of 2 values. [f] INGAMELLS AND SUHR[24], one value except syenite-1 (mean of 3 values).

Comparison of results on geochemical standards

Comparative analyses for fluorine and chlorine on a variety of standard silicates by different analytical techniques are given in Table V. The chlorine results show good agreement within the experimental error of the chemical method, whereas the comparison of fluorine results show even better agreement. Since the fluorine contents in T-1, Syenite-1, GR, and S-1 found here are virtually the same as those reported by INGAMELLS AND SUHR[24], and THOMAS AND KEMPE[25], and KORITNIG[26], it is unlikely that any gross error is present in this method.

TABLE VI

DETERMINATION OF FLUORINE AND CHLORINE IN SOME STANDARD SILICATE ROCKS

Sample	*Fluorine*							*Chlorine*						
	Found (p.p.m.)				*Mean (p.p.m.)*	*Std. devn.*	*C*[a] *(%)*	*Found (p.p.m.)*				*Mean (p.p.m.)*	*Std. devn.*	*C*[a] *(%)*
G-1 (Granite)	710	715	690	—	705	13.2	1.87	65	61	64	—	63	2.1	3.3
W-1 (Diabase)	210	205	210	210	208	2.65	1.27	184	185	188	190	187	2.76	1.48
S-1 (Shale)	885	870	880	900	884	9.11	1.03	70	74	74	71	72	2.1	2.9
Syenite-1	1800	1740	—	—	1770	42.4	2.40	215	225	—	—	220	7.07	3.21
T-1 (Tonalite)	400	380	—	—	390	14.1	3.62	130	125	—	—	128	3.61	2.82
GR (Granite)	910	940	—	—	925	22.4	2.42	310	320	—	—	315	7.07	2.24
GA (Granite)	430	450	—	—	440	14.1	3.20	303	295	—	—	299	5.65	1.89
GH (Granite)	4600	4500	—	—	4550	70.71	1.55	510	495	—	—	503	10.6	2.10
G-2 (Granite)	1220	1190	—	—	1205	22.36	1.86	194	188	—	—	192	4.47	2.33
GSP-1 (Granodiorite)	1880	2000	—	—	1940	84.85	4.37	333	350	—	—	342	12.0	3.51
AGV-1 (Andesite)	440	430	—	—	435	7.07	1.63	323	315	—	—	319	5.66	1.77
BCR-1 (Basalt)	480	490	—	—	485	7.07	1.46	61	63	—	—	62	1.4	2.3
DTS-1 (Dunite)	14	10	—	—	12	2.8	23.3	35	31	—	—	33	2.8	8.5
PCC-1 (Perodotite)	14	11	—	—	13	2.8	21.5	70	75	—	—	74	4.6	6.2
NBS-4999 (Dunite)	46	50	—	—	48	2.8	5.9	105	106	—	—	106	1.00	0.94

[a] Relative deviation of reproducibility in %.

Fifteen standard rock samples containing widely varying amounts of fluorine and chlorine were analyzed in replicate by this method. The results as shown in Table VI are very satisfactory. The precision of this method was generally better than 5% and lower at higher concentrations.

The color of the iron(III) thiocyanate complex fades in light, which catalyzes the oxidation of thiocyanate by iron(III). Consequently the absorbance measurement for chlorine analyses should be made within 30 min after mixing.

Fluorine analyses require no added manipulations to remove interferences and provide a rapid and simple procedure for handling a large number of analyses. This approach of simultaneous determination of fluorine and chlorine would appear to have wide applicability to many kinds of silicate rocks. Where a large number of analyses are to be made, 10 analyses for fluorine and chlorine can be completed each day.

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SUMMARY

A rapid accurate method is described for simultaneous determination of fluorine and chlorine in silicate rocks by taking separate aliquots of the single sample dissolution. Fluorine, without separation, was determined by means of the zirconium–eriochrome cyanine R complex, whereas chlorine was determined by means of the stable iron(III) thiocyanate complex. The method was tested with standard rocks. Results with geochemical standards were comparable with analyses reported by others. Application to several acidic, mafic, and ultramafic rock samples gave results with a relative standard deviation of less than 5 %.

RÉSUMÉ

On propose une méthode rapide et précise pour le dosage simultané du fluor et du chlore dans des roches silicatées, en prélevant des parties aliquotes sur une seule solution de l'échantillon. Le fluor est dosé, sans séparation au moyen du complexe zirconium ériochrome cyanine R, tandis que le chlore est dosé à l'aide du complexe coloré stable fer(III)–thiocyanate. Ce procédé, éprouvé avec des roches étalon, a été appliqué à plusieurs échantillons de roches, donnant des résultats excellents, avec une déviation standard relative de moins de 5%.

ZUSAMMENFASSUNG

Eine schnelle und genaue Methode zur gleichzeitigen Bestimmung von Fluor und Chlor in Silikaten wird beschrieben. Es werden dabei getrennte, aliquote Teile von nur einer gelösten Probe genommen. Fluor wurde ohne Trennung mit Zirkonium–Eriochrom–Cyanin R, Chlor mit dem stabilen Eisen(III)-Thiocyanatkomplex bestimmt. Die Probe wurde mit Standardgesteinen geprüft. Ergebnisse mit geochemischen Standards waren vergleichbar mit Analysen anderer Autoren. Verschiedene Proben ergaben Standardabweichungen von < 5%.

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QUINOLINIUM AND LUTIDINIUM MOLYBDATES AS REAGENTS FOR THE PRECIPITATION OF PHOSPHATE

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Organic base molybdates have often been used to determine phosphorus, and methods involving the precipitation of quinolinium molybdophosphate are increasing in popularity.

Radiochemicals are applicable to the study of existing methods for the determination of phosphorus, and are of assistance in formulating new ones. Investigations previously carried out in this laboratory have been concerned with the ammonium molybdophosphate method for the determination of phosphorus[1-3]. In the present investigation phosphorus-32 and arsenic-74 have been used to study the precipitation of quinolinium molybdophosphate and to examine lutidinium molybdates as reagents for precipitating phosphorus.

Quinoline was proposed as a reagent for phosphorus by WILSON[4]. He did not succeed in obtaining a satisfactory gravimetric finish to the determination but found that quinoline was a sufficiently weak base not to interfere in a volumetric method. However, PERRIN[5] and LENCH[6] succeeded in applying a gravimetric finish. WENDLANDT AND HOFFMAN[7] have studied the determination using thermogravimetric and differential analysis. Since WILSON first introduced the method, only minor modifications have been suggested. FERNLUND *et al.*[8] and LENCH[6] preferred to add a prepared reagent instead of adding the reagents separately. ALFELT[9] showed that hydrochloric, nitric and perchloric acids were suitable for the precipitating medium but, like most other workers, imposed upper limits on the acidity which could be tolerated. Most workers appear to prefer an acidity of about 1 *M* for the precipitation but report that precipitation is perfectly satisfactory from hydrochloric acid as strong as 1.6 *M*.

The effect of foreign ions on the precipitation of quinolinium molybdophosphate has been investigated by WILSON[4], FERNLUND AND ZECHNER[10], ALFELT[9] and LENCH[6]. WILSON and FERNLUND AND ZECHNER, working with appreciable amounts of phosphorus, found that iron had no effect on the precipitation. Later investigators have found that iron exerts a marked inhibitory effect when the phosphorus content is small. The inhibition can be reduced by digesting the solution for longer than the normal period and also by the addition of larger amounts of reagent.

MEYER AND KOCH[11] and LENCH[6] have found that quinolinium molybdoarsenate is coprecipitated with quinolinium molybdophosphate under all conditions of precipitation. LENCH applied the method to a variety of standard metallurgical samples but in some cases the results differed considerably from the accepted values.

Lutidinium molybdates have not previously been examined as precipitants for phosphate.

EXPERIMENTAL AND RESULTS

Solutions

Phosphate solutions. Dried potassium dihydrogen phosphate (Analar grade, 0.128 g) and about 40 μC of the radioisotope phosphorus-32, which was obtained as orthophosphate, were diluted to 100 ml with water. An unlabelled solution containing 1.28 g of dried potassium dihydrogen phosphate per litre was also used in some experiments.

Arsenate solutions. Disodium hydrogen arsenate heptahydrate (Analar grade, 0.293 g) and about 40 μC of arsenic-74, which was obtained as sodium arsenate, were diluted to 100 ml with water. An unlabelled solution containing 2.93 g of disodium hydrogen arsenate heptahydrate per litre was also used in some experiments.

Quinolinium molybdate reagent. The reagent was prepared by the method advocated by LENCH[6]. Analar grade molybdenum trioxide (150 g) was added to a solution of sodium hydroxide (50 g) in 600 ml of water, heated until dissolved and then allowed to cool. Concentrated hydrochloric acid (500 ml) was added, heated to dissolve the precipitate, and the solution was cooled. Hydrogen peroxide (100-vol) was added dropwise until the green colour was removed. Freshly distilled quinoline (28 ml) was dissolved in 600 ml of hydrochloric acid (50%). The two solutions were mixed, heated to boiling, and allowed to stand at room temperature for 24 h. The solution was diluted to 2 l and filtered into a plastic bottle.

2,6-Lutidinium molybdate reagent. 2,6-Lutidine (36 ml), which had been purified by fractionation, was used to prepare 2 l of lutidinium molybdate solution by the method described for quinolinium molybdate.

2,4- and 2,5-Lutidinium molybdate reagent. A mixture of 2,4- and 2,5-lutidine was fractionated several times in order to prepare a fraction rich in 2,4-lutidine (b.p. 157.8) and a fraction rich in 2,5-lutidine (b.p. 159.6). These fractions were used to prepare 2,4- and 2,5-lutidinium molybdates by the method described for quinolinium molybdate.

Solutions containing transition-metal ions. Six solutions of iron(III) nitrate were prepared, each containing, per l, 1.28 g of dried potassium dihydrogen phosphate and sufficient iron(III) nitrate to give solutions containing Fe^{3+} and PO_4^{3-} in the molar ratio of 10, 25, 50, 75, 100 and 150 to 1, respectively.

Solutions containing chromium(III) nitrate or manganese(II) nitrate or nickel(II) nitrate were prepared in the same way as the iron(III) solutions.

Hydrochloric acid wash solution. A 2% solution was prepared.

Solvent mixture. Aqueous ammonia (s.g. 0.88), acetone and water were mixed in the ratio of 1:20:20.

Details of the counting equipment, temperature control and sintered glass filters were given in a previous paper[3].

Distilled water is implied in the directions for the preparation of solutions.

Both radiochemicals used in these experiments were obtained from the Radiochemical Centre, Amersham.

Conditions for the quantitative precipitation of phosphate as quinolinium 12-molybdophosphate

The following general procedure was used in all experiments except where otherwise stated.

Quinolinium molybdate was added dropwise to a boiling solution of potassium dihydrogen phosphate. Distilled water was added so that the total volume of the solution was about 10 ml when precipitation occurred. The solution was maintained at the boiling point for 10 min and at room temperature for the same period of time. The yellow precipitate of quinolinium molybdophosphate was filtered, and washed with 2 % hydrochloric acid and then with water. A count was taken on the combined filtrate and washings and on an acetone–aqueous ammonia extract of the quinolinium molybdophosphate. The percentage precipitation was calculated from the corrected count-rates.

The effect of adding an excess of the quinolinium molybdate reagent. Quinolinium molybdate was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 μC phosphorus-32. The percentage of phosphorus precipitated was calculated (Table I).

TABLE I

THE EFFICIENCY OF PRECIPITATION OF QUINOLINIUM 12-MOLYBDOPHOSPHATE

(Solution maintained at boiling point for 10 min)

Amount of quinolinium molybdate added (ml)	*Stoichiometric ratio of molybdate to phosphate (12Mo:1P = 1)*	*% Efficiency*
0.5	1.0	99.31
0.75	1.5	99.77
1.0	2.0	99.91
1.5	3.0	99.92
2.0	4.0	99.93
5.0	10.0	99.96

TABLE II

THE EFFECT OF TEMPERATURE

(Solution maintained at the selected temperature for 10 min)

Precipitation temperature (°)	*Phosphorus precipitated (%)*	*Precipitation temperature (°)*	*Phosphorus precipitated (%)*
60	98.62	90	99.86
70	99.35	Boiling point	99.93
80	99.71		

The temperature necessary for quantitative precipitation of phosphate. Quinolinium molybdate (2 ml) was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 μC phosphorus-32, in a series of experiments at different temperatures. The percentage of phosphorus precipitated was calculated (Table II).

The time necessary for quantitative precipitation of phosphate. Quinolinium molybdate (2 ml) was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 µC phosphorus-32. When the solution was maintained at its boiling point for 4 min the precipitation was quantitative, 99.86% of the phosphate present being precipitated. After 10 min the amount of precipitation was 99.93%; after 2 h it was 99.96%.

The effect of acid on the precipitation. Quinolinium molybdate (2 ml) was added to potassium dihydrogen phosphate (2 ml) and varying amounts of hydrochloric acid. The percentage of phosphorus precipitated was calculated (Table III).

TABLE III

THE EFFECT OF HYDROCHLORIC ACID ON THE PRECIPITATION OF PHOSPHATE AS QUINOLINIUM 12-MOLYBDOPHOSPHATE

(Solution maintained at boiling point for 10 min)

Amount of HCl (s.g. 1.18) added (ml)	*Final molarity of HCl*	*Phosphorus precipitated (%)*
1	1.88	99.93
2	2.50	99.91
3	3.39	99.79
4	3.95	99.40
5	4.47	98.88

The amount of arsenate precipitated. Quinolinium molybdate (2 ml) was added to potassium dihydrogen phosphate (2 ml) and sodium arsenate containing about 0.5 µC arsenic-74/ml. Arsenate equimolar with phosphate was quantitatively precipitated.

The effect of iron(III) nitrate on the precipitation of phosphate. Quinolinium molybdate (2 ml) was added to a solution (2 ml) containing radioactive phosphate and inactive iron(III) nitrate. In a series of experiments the Fe^{3+}/PO_4^{3-} ratio was varied from 10 to 150.

When the Fe^{3+}/PO_4^{3-} ratio was 25, only 99.67% of the phosphate was precipitated; when it was 50 only 93.81%; above 75 the precipitate passed through the filter. In every case a 2-h digestion near the boiling point resulted in quantitative precipitation of phosphate, that is, more than 99.80% of the phosphorus appeared in the precipitate.

The effect of iron(III) nitrate and phosphate on the precipitation of arsenate. Quinolinium molybdate (2 ml) was added to an iron(III) nitrate solution (2 ml) containing inactive phosphate and active arsenate (2 ml) (*ca.* 0.5 µC arsenic-74). The amounts of arsenate and phosphate taken were equimolar for each test. In a series of experiments the Fe^{3+}/PO_4^{3-} (AsO_4^{3-}) ratio was varied from 10 to 150. The percentage of arsenic precipitated was calculated.

When the Fe^{3+}/PO_4^{3-} (AsO_4^{3-}) ratio was 10, only 94.20% of the arsenic was precipitated; when the ratio was 25 or above the precipitate passed through the filter. In every case a 2-h digestion near the boiling point gave an easily filterable precipitate in which the arsenate was quantitatively precipitated.

The effect of chromium(III) nitrate, manganese(II) nitrate and nickel(II) nitrate on the precipitation of phosphate. Quinolinium molybdate (2 ml) was added to a chromium(III) nitrate solution (2 ml) containing active phosphate (*ca.* 0.5 μC phosphorus-32). A series of experiments was carried out in which the Cr^{3+}/PO_4^{3-} ratio varied from 10 to 150. The percentage of phosphorus precipitated was calculated.

This experiment was repeated with manganese(II) nitrate/phosphate and with nickel(II) nitrate/phosphate solutions. The results are shown in Table IV.

The effect of chromium(III) nitrate, manganese(II) nitrate, nickel(II) nitrate and phosphate on the precipitation of arsenate. Quinolinium molybdate (2 ml) was added to a chromium(III) nitrate solution (2 ml) containing phosphate and active sodium arsenate (2 ml) (*ca.* 0.5 μC arsenic-74). In a series of experiments the Cr^{3+}/PO_4^{3-} (AsO_4^{3-}) ratio was varied from 10 to 150.

TABLE IV

THE EFFECT OF SOME TRANSITION-METAL IONS ON THE PRECIPITATION OF PHOSPHATE

(Solution maintained at boiling point for 10 min)

Element added as nitrate	*Molar ratio metal/phosphorus*					
	10	*25*	*50*	*75*	*100*	*150*
	Phosphorus precipitated (%)					
Cr	99.91	99.82	99.68	99.53	99.36	99.03
Mn	99.93	99.91	99.89	99.87	99.85	99.81
Ni	99.92	99.89	99.85	99.82	99.77	99.70

TABLE V

THE EFFECT OF PHOSPHATE AND SOME TRANSITION-METAL IONS ON THE PRECIPITATION OF ARSENATE

(Solution maintained at boiling point for 10 min)

Element added as the nitrate	*Molar ratio metal/arsenic*					
	10	*25*	*50*	*75*	*100*	*150*
	Arsenic precipitated (%)					
Cr	99.69	99.30	99.81	98.02	97.23	96.20
Mn	99.79	99.74	99.61	99.42	99.23	98.94
Ni	99.80	99.71	99.58	99.37	99.05	98.70

The experiment was repeated with manganese(II) nitrate/phosphate and with nickel(II) nitrate/phosphate solutions. The results are shown in Table V.

The precipitation of phosphate as 2,4-, 2,5- and 2,6-lutidinium molybdophosphates

Initial experiments with the 3 isomers of lutidine under investigation showed that at any temperature in the range 5–100° phosphate was immediately precipitated. Little difference was found in the amount of phosphorus precipitated when either 2,4-, 2,5-, or 2,6-lutidinium molybdate was used as a precipitant under a given set of conditions. This was not the case for arsenate since 2,4-lutidinium molybdate precipitated arsenate more readily than either the 2,5- or the 2,6-isomer; 2,6-lutidinium molybdoarsenate was the least readily precipitated. Below room temperature a considerable time elapsed before a precipitate was formed, and at 5° a solution containing arsenate and 2,6-lutidinium molybdate showed no signs of any turbidity after 30 min. 2,6-Lutidinium molybdate was chosen for further trials with a view to achieving a separation of phosphate–arsenate mixtures.

2,6-Lutidinium molybdate (2 ml) was added to potassium dihydrogen phosphate (2 ml) containing about 0.5 μC phosphorus-32, in a series of experiments at different temperatures. The solution was stirred intermittently and maintained at the selected temperature for a known length of time. When the solution was maintained below room temperature, it was filtered immediately after removal from the thermostat. If the solution was maintained above room temperature, it was allowed to cool before it was filtered. The yellow precipitate of 2,6-lutidinium molybdophosphate filtered easily and was washed with 2 % hydrochloric acid and then with water.

A count was taken on the combined filtrate and washings and on the acetone–aqueous ammonia extract of the lutidinium molybdophosphate. The percentage of phosphorus precipitated was calculated from the corrected count-rates (Table VI).

When the precipitation was carried out at the boiling point, the precipitate contained specks of blue.

TABLE VI

THE EFFECT OF TEMPERATURE AND STANDING TIME ON THE PRECIPITATION OF 2,6-LUTIDINIUM MOLYBDOPHOSPHATE

Precipitation temperature (°)	*% Phosphorus precipitated*			
	Time (min)	*10*	*20*	*30*
5		71.4	82.6	85.2
10		96.9	97.4	97.9
15		98.0	98.1	98.1
20		98.1	98.2	98.2
30		98.1	—	—
40		98.1	—	—
50		98.3	98.4	98.3
Boiling point		98.4	—	—

TABLE VII

THE EFFECT OF TEMPERATURE AND STANDING TIME ON THE PRECIPITATION OF 2,6-LUTIDINIUM MOLYBDOARSENATE

Precipitation temperature (°)	*% Arsenic precipitated*			
	Time (min)	*10*	*20*	*30*
5		None	None	None
10		None	1.2	3.7
15		None	2.5	6.0
20		6.2	—	—

The precipitation of arsenate as 2,6-lutidinium molybdoarsenate

2,6-Lutidinium molybdate (2 ml) was added to disodium hydrogen arsenate (2 ml) containing about 0.5 μC arsenic-74 in a series of experiments similar to those carried out on phosphate. The percentage of arsenic precipitated in the green precipitate of 2,6-lutidinium molybdoarsenate was calculated from the corrected count-rates (Table VII).

When 2,6-lutidinium molybdate (2 ml) was added to a mixture containing equimolar amounts of phosphate (2 ml) and arsenate (2 ml), tracer studies showed that at temperatures in the range 10–15° the amount of phosphate precipitated after 10 minutes was 96–98%. The precipitate contained less than 0.1% arsenic.

DISCUSSION

Quinolinium molybdate

When quinolinium molybdate is added dropwise to a boiling solution containing phosphate, the radiochemical studies confirmed that phosphorus can be quantitatively precipitated as quinolinium molybdophosphate using the reagent described by LENCH[6], which is very similar to that of FERNLUND AND ZECHNER[10]. If the solution is maintained at the boiling point for 10 min, 99.3% of the phosphorus present is precipitated by the stoichiometric amount of quinolinium molybdate. In order to ensure quantitative precipitation of phosphorus and to minimise inhibitory effects of interfering ions, a 4-fold excess of reagent is desirable in routine work.

At a temperature of 70°, 99.35% of the phosphorus present was precipitated after 10 min, although more would probably have been precipitated had a longer time been allowed for precipitation. The precipitation of quinolinium molybdophosphate at the boiling point shortens the time required for the determination of phosphorus and gives an easily filterable precipitate. When the solution is maintained at the boiling point for 10 min with a 4-fold excess of quinolinium molybdate, 99.93% of the phosphorus present can be precipitated as quinolinium molybdophosphate. The deep-yellow precipitate shows no visible evidence of molybdic acid.

Hydrochloric acid has less effect on the precipitation of quinolinium molybdophosphate than on that of ammonium molybdophosphate. Hydrochloric acid up to 2.5 *M* was found to have no effect on the precipitation, which is in good agreement with the results obtained by WILSON[4]. At 4.47 *M*, 98.88% of the phosphorus is precipitated.

Under the conditions employed for the precipitation of phosphorus, arsenic is quantitatively precipitated as quinolinium molybdoarsenate. Consequently the complete removal of arsenic is essential in the determination of phosphorus.

Iron(III) nitrate inhibits the precipitation of quinolinium molybdophosphate and increases the time required for the quantitative precipitation of phosphorus. When the Fe^{3+}/PO_4^{3-} ratio is 25, 99.67% of the phosphorus is removed from solution; if only 10 min are allowed for the precipitation, the precipitate passes through the filter when the Fe^{3+}/PO_4^{3-} ratio is higher than 75. In the presence of dissolved iron, the precipitate is still in a finely divided form after 10 min at boiling point, but a 2-h digestion near the boiling point is sufficient to precipitate phosphorus quantitatively in a filterable form, even if the Fe^{3+}/PO_4^{3-} ratio reaches 150.

The effect of iron(III) nitrate on the precipitation of arsenate is similar to that on phosphate, but more pronounced. When the Fe^{3+}/PO_4^{3-} ratio and the Fe^{3+}/AsO_4^{3-} ratio is 10, only 94.2% of the arsenic is precipitated, and when the ratio is above 25, the precipitate passes through the filter. Again, a 2-h digestion near boiling point gives an easily filterable precipitate in which arsenate is quantitatively precipitated, even when the Fe^{3+}/PO_4^{3-} (AsO_4^{3-}) ratio reaches 150.

Chromium(III) nitrate, manganese(II) nitrate and nickel(II) nitrate have relatively little effect on the precipitation of quinolinium molybdophosphate. If the precipitate is maintained at the boiling point for 10 min, metal ion/phosphate ratios of 25, 75 and 150 for chromium(III), nickel(II) and manganese(II) nitrate solutions, respectively, can be tolerated while quantitative precipitation of phosphorus is still achieved. Increasing all 3 metal ion/phosphate ratios up to 150 still results in over 99% precipitation of phosphorus in each case.

The effect of chromium(III), manganese(II) and nickel(II) nitrates on the precipitation of arsenate is small, even in the presence of an equimolar amount of phosphate.

In conclusion, it can be said that since quinolinium molybdate can be used at the boiling point, phosphate is precipitated quickly. The precipitation is less inhibited by transition-metal ions and acid anions than the precipitation of ammonium molybdophosphate. Ions such as arsenate, which form insoluble complex molybdates, are readily precipitated by quinolinium molybdate and must be completely removed before the determination of phosphorus.

Lutidinium molybdate

The 2,4-, 2,5- and 2,6-isomers of lutidine can be used to form a reagent which precipitates phosphate as lutidinium molybdophosphate. The most useful reagent is 2,6-lutidinium molybdate because it precipitates arsenate less readily than the other isomers, but still precipitates phosphate reasonably quickly.

At 10°, 96.9% of the phosphorus present is removed from solution in 10 min by the addition of a four-fold excess of 2,6-lutidinium molybdate; at 15°, 98.0% of the phosphorus is precipitated, while at the boiling point the percentage precipitation increases to 98.4.

If only 10 min are allowed for the precipitation at temperatures up to 15°, arsenate is not precipitated by 2,6-lutidinium molybdate; if 20 min are allowed for the precipitation, 1.2% and 2.5% of the arsenic present is precipitated at 10° and 15° respectively. Above 15° the precipitation of arsenic increases rapidly.

At temperatures higher than 15°, there is little increase in the efficiency of precipitation of phosphorus, the upper limit of about 98% probably being determined by the solubility of the precipitate. A high precipitation temperature would reduce the length of time necessary for the precipitation, but since the precipitate is reduced, and since arsenate is also rapidly precipitated at higher temperatures, a temperature of 15° appears to be the most useful one for the precipitation of 2,6-lutidinium molybdophosphate. The reagent is not as efficient as quinolinium molybdate for the precipitation of phosphate, but the fact that phosphorus and arsenic can be separated by 2,6-lutidinium molybdate may be useful.

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SUMMARY

The precipitation of phosphate with quinolinium molybdate was studied by means of radioactive tracers, in relation to the excess of reagent, temperature of precipitation, etc. Precipitation is almost quantitative (99.3%) even with a stoichiometric amount of reagent added but an excess helps to minimise the inhibitory effects

of certain ions, notably Fe^{3+}; inhibitory effects are eliminated by digesting the solution for 2 h. Chromium(III) nitrate, nickel(II) nitrate and manganese(II) nitrate have relatively little effect on the precipitation of quinolinium molybdophosphate. Under the conditions required for the quantitative precipitation of phosphorus, arsenic is also quantitatively precipitated.

Phosphate can be precipitated as lutidinium molybdophosphate using 2,4-, 2,5- or 2,6-lutidinium molybdate; the reagents are less efficient than quinolinium molybdate but can be used to precipitate phosphate under conditions which leave arsenate in solution.

RÉSUMÉ

On a examiné la précipitation des phosphates au moyen de molybdate de quinolinium à l'aide de traceurs radioactifs. La réaction est presque quantitative (99.3%) même avec des quantités stoechiométriques de réactif; cependant un excès permet de diminuer l'influence inhibitrice de certains ions, notamment Fe^{3+}. Les nitrates de chrome(III), de nickel et de manganèse ont relativement peu d'effet sur la précipitation. L'arsenic précipite quantitativement. Le molybdate de 2,6-lutidinium permet de précipiter les phosphates tout en maintenant les arséniates en solution.

ZUSAMMENFASSUNG

Die Fällung von Phosphat mit Chinolin-Molybdat wurde mittels radioaktiven Tracern untersucht, und zwar in Abhängigkeit vom Reagenz-überschuss, der Fällungstemperatur usw. Die Fällung ist nahezu quantitativ (99.3%) sogar mit der stöchiometrischen Reagenzmenge. Verzögerungseffekte werden durch zweistündiges Kochen oder durch einen Überschuss des Reagenzes eliminiert. Chrom(III)-nitrat, Nickel(II)-nitrat und Mangan(II)-nitrat haben einen relativ geringen Einfluss auf die Fällung. Arsen wird ebenfalls quantitativ gefällt. Phosphat kann ferner mit 2,4-, 2,5- oder 2,6-Lutidin-Molybdat gefällt werden. Diese Reagenzien sind jedoch weniger wirksam als das Chinolin-Molybdat. 2,6-Lutidin-Molybdat kann jedoch verwendet werden, um das Phosphat unter Bedingungen zu fällen, bei denen Arsenat in Lösung bleibt.

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THE DETERMINATION OF PHOSPHORUS WITH ORGANIC BASE MOLYBDATES

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The classical determination of phosphorus involves precipitation of ammonium phosphomolybdate, but many organic bases have been examined as alternatives to the ammonium ion[1]. Of these, by far the most satisfactory is quinoline, which was first introduced by WILSON[2] and has been applied for various purposes by many later workers[1]. The main disadvantage in the use of quinoline is the interference of arsenate and silicate ions. Arsenate can, in fact, be determined in the same way as phosphate, although the conditions require stricter control because of the greater solubility of the arsenomolybdate precipitate[3]. Silicate can also be determined with quinoline molybdate, both titrimetric[4] and gravimetric[5,6] finishes being feasible.

It is possible to determine phosphate in the presence of silicate if citric acid is added to prevent the formation of silicomolybdate, but the formation of phosphomolybdate may also be affected if the concentration of citric acid is not strictly controlled. Citric acid only partially prevents the formation of arsenomolybdate.

Quinoline phosphomolybdate has been utilized for the determination of milligram[7] and microgram[8] amounts of phosphorus in organic compounds; particularly on the microgram scale, very strict control is necessary to avoid incomplete formation of the precipitate in the presence of the complexing agent needed to keep silicate in solution.

The work described below was undertaken primarily to find an organic base which would retain the favorable properties of quinoline while providing a less soluble phosphomolybdate with more soluble arseno- and silicomolybdates. Of the many bases tested, the best proved to be α-picoline (2-methylpyridine), which largely fulfils the above demands.

Qualitative testing of organic bases

Initial sensitivity tests were carried out under the general conditions which give satisfactory precipitation of quinoline phosphomolybdate. Phosphate, arsenate and silicate were tested at acidities of 0.5, 1.0 and 2.0 M in hydrochloric acid; the bases, which were not specially purified before use, were regarded as unreactive if no precipitate was formed with *ca.* 0.5 mg/ml of the element under test in the final solution.

The following simple bases gave no reaction: ethanolamine, diethanolamine, triethanolamine, di(m)ethylamine, butylamine, guanidine, aminomercuric (chloride),

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piperidine and *o*-phenetidine. Many of the alkylamines had been tested for precipitation of phosphomolybdate by SONNENSCHEIN[9] who reported precipitate formation in some cases. The following bases gave visible precipitates with 5–10 μg P/ml but not with arsenate or silicate: benzotriazole, choline, melamine, tetramethylamine and hexamine (the last only in acetic acid media). However, the sensitivity is obviously too low for quantitative work.

This preliminary screening[10] showed that the bases: tri-*n*-butylamine, di-*n*-butylamine, 2- and 3-methylpyridine, pyridine, 8-hydroxyquinoline, acridine and phenazone were the only ones worth examining further. Later tests gave the results shown in Table I. The results for quinoline are given for comparison; 8-hydroxyquinoline, which has also been widely used[1], behaved similarly to quinoline, but is undesirable because of uncertainties about the actual composition of the precipitate. Di-*n*-butylamine and acridine formed unstable reagent solutions and were not examined further. WILSON[2] found pyridine phosphomolybdate too soluble even for macrodeterminations, though the rough tests carried out here were more in line with the results of VORTMANN[11] who suggested the reagent. However, the methylpyridines seemed much more promising and were examined quantitatively along with phenazone and tributylamine.

TABLE I

SENSITIVITY TESTS FOR PHOSPHATE, ARSENATE AND SILICATE

Base tested	*Visible precipitate formed with (µg/ml)*		
	P	*As*	*Si*
Di-*n*-butylamine	1	No ppt.	No. ppt.
Tri-*n*-butylamine	0.5	5	5
Pyridine	1	No ppt.	No ppt.
α-Picoline	0.25	5	5
β-Picoline	0.25	5	5
Quinoline	0.5	0.5	0.5
Acridine	0.5	5	5
Phenazone	0.5	5	5

Quantitative testing of organic bases

Phenazone (antipyrine) has been studied[12] for the precipitation of silicomolybdate but not of phosphomolybdate; the precipitates obtained in the present work proved difficult to filter and wash so that the phosphorus results were very variable. Similar though slighter troubles were found in filtering the tri-*n*-butylamine precipitates; variations in precipitation conditions to improve the physical characteristics of the precipitate were unsuccessful. Moreover, the precipitates were difficult to dissolve in sodium hydroxide solution for the titrimetric finish and poor phenolphthalein end-points were obtained; both of these faults were probably caused by the strong basicity of tri-*n*-butylamine. α-Picoline and β-picoline both gave clear yellow phosphomolybdate precipitates which were easy to filter, wash and dissolve in sodium hydroxide solution. The precipitate formed with β-picoline had a slight tendency to pass through the filter and all further work was therefore done with α-picoline.

α-Picoline as a reagent for quantitative precipitation of phosphate

The main interest in this work was the development of an improved microdetermination of phosphorus, and so the range 0.2–1 mg of phosphorus (as potassium hydrogen phosphate) was examined. The procedure was essentially the same as that used previously with quinoline as the base reagent[7]. The conversion factor used for quinoline, which is based on the consumption of 26 equivalents of sodium hydroxide in dissolving the quinoline phosphomolybdate precipitate, proved unsatisfactory, but excellent results (Table II) were obtained when the calculations were based on the consumption of 23 equivalents as in the case of ammonium phosphomolybdate.

TABLE II

DETERMINATION OF PHOSPHATE AS α-PICOLINE PHOSPHOMOLYBDATE

P taken (mg)	*No. of detns.*	*Av.P found (mg)*	*Range of errors*[a]
0.185	5	0.185	−2.7 to +1.6
0.370	4	0.370	−1.6 to +0.8
0.556	3	0.557	−0.5 to +1.4
0.741	3	0.743	−0.2 to +1.2
0.927	3	0.923	−1.2 to +0.2

[a] Expressed as the relative percentage deviation from the theoretical.

The empirical equation[13]:

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 + 23\ NaOH \rightarrow 11\ Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11\ H_2O$$

fits the facts for ammonia, as does the equation:

$$(C_9H_7N)_3H_3PO_4 \cdot 12\ MoO_3 + 26\ NaOH \rightarrow 12\ Na_2MoO_4 + Na_2HPO_4 + 3\ C_9H_7N + 14\ H_2O$$

given by WILSON[2], for quinoline. It is surprising that α-picoline (pK value 5.95)[14] should behave more like ammonia (pK 9.24) than like quinoline (pK 4.9)[14]; potentiometric titrations showed, however, that the literature pK values are at least approximately correct. In all 3 cases, the phenolphthalein end-points are quite clear. Since the actual reaction of the base phosphomolybdates with alkali is obscure and undoubtedly complicated, the factor used in the present work was based on the experimental data found, which correspond to a dissolution process analogous to that of the ammonium complex.

The gravimetric behaviour of the α-picoline precipitate also differed from that of quinoline. Quinoline phosphomolybdate can be weighed as the anhydrous complex after being dried at 160° or as the dihydrate after being washed with dioxan and ether[15]; WENDLANDT AND HOFFMAN[16] confirmed the drying temperature of 160° but suggested that a monohydrate is actually precipitated. However, with α-picoline, the anhydrous complex seemed to be precipitated and could be weighed, though not with sufficient accuracy for microgravimetric purposes, after being washed with dioxan and ether. The composition of the precipitate after drying at 110° or 160° corresponded to no definite formula. Thermogravimetric analysis indicated a gradual loss in weight up to 320° at which temperature the complex decomposed very rapidly;

the removal of the organic base was complete at about 500°, *i.e.* at the same temperature as for the quinoline precipitate[16].

Further tests of the titrimetric procedure were made with separate additions of the α-picoline and molybdate reagents, and with addition of a single solution containing both reagents, as recommended for quinoline by FERNLUND AND ZECHNER[17]. There was no difference in accuracy for the 2 techniques. The single reagent solution was used in all further work. It could be stored for a period up to one month, whereas the useful life of a mixed quinoline reagent is only about one week.

As in the case of quinoline, neither the temperature of the precipitation nor the time of standing before filtration was important when α-picoline molybdate was used as precipitant.

Interferences

Only brief tests were made of cationic interferences, because the procedure was intended ultimately for application to organic compounds. There was no interference from 500-mg amounts of zinc acetate, iron(III) sulphate or titanium(IV) sulphate when 0.5 mg of phosphorus was determined; 500 mg of aluminium potassium sulphate or lead acetate caused *ca.* 20% low recoveries. There was no interference from 500-mg amounts of fluoride, bromide, nitrate or sulphate in the precipitation of 0.2–0.5 mg of phosphorus; iodide interfered by reducing the precipitate, but this reaction would not intervene in organic analysis by the decomposition method used, where organic iodine would be converted to iodate.

Citric acid is normally added before precipitation of quinoline phosphomolybdate to prevent interference of silicate[2] but, at least for the microdetermination, more than 100 mg of citric acid also affects the precipitation of the phosphomolybdate[7]. The precipitation of α-picoline phosphomolybdate was found to be much less affected by citric acid, up to 700 mg being without influence on the precipitation of 0.5 mg of phosphorus. This tolerance, combined with the comparative lack of sensitivity of α-picoline for arseno- and silicomolybdate, made it possible to determine phosphorus in

TABLE III

DETERMINATION OF PHOSPHORUS IN PRESENCE OF ARSENIC AND SILICON

Interfering element	*Amount added (mg)*	*Amount of citric acid added (mg)*	*P taken (mg)*	*P found (mg)*
Arsenic	0.5	—	0.459	0.567, 0.554
	0.5	200	0.459	0.459, 0.455
	—	200	0.459	0.460, 0.456
	1.0	200	0.459	0.533, 0.553
	1.0	500	0.459	0.461, 0.464
	—	500	0.459	0.458, 0.455
	3.0	500	0.459	0.498, 0.501
	3.0	700	0.459	0.462, 0.460
	—	700	0.459	0.458, 0.453
Silicon	2.0	500	0.459	0.456, 0.455
	3.0	500	0.459	0.508
	3.0	700	0.459	0.454, 0.452
	5.0	700	0.459	0.454, 0.458

the presence of relatively large amounts of arsenate and silicate. Even 0.5 mg of arsenic or silicon caused high phosphorus recoveries in the absence of citric acid because of coprecipitation, but up to 3 mg and 5 mg respectively had no effect on the results in the presence of 700 mg of citric acid (Table III).

Application to organic compounds

The conventional oxygen-flask method as described previously[7] for phosphorus with alkaline hypobromite as absorbing solution was used to decompose the samples. The α-picoline reagent proved generally more convenient than the quinoline used previously. Although citric acid was still necessary to prevent interference from silicate from the flask wall, its amount was not at all critical. When the sample contained fluorine, no addition of boric acid was needed to prevent excessive attack of hydrogen fluoride on the flask wall, which in the quinoline method produced more silicate than could be held in solution by the highest tolerable amount of citric acid. Results for a series of standard and research compounds are shown in Table IV.

TABLE IV

ANALYSIS OF ORGANIC COMPOUNDS

Compound	*Amount taken (mg)*	*P present (%)*	*P found (%)*
Triphenylphosphate (8 results)	3.3–7	9.52	9.53 ± 0.17
Triphenylphosphate + 10 mg arsanilic acid		9.52	9.67, 9.39
Triphenylphosphine (7 results)	3.2–6.5	11.81	11.79 ± 0.26
Research compound[a]	5.282	7.20	7.46
Research compound[a]	3.196	9.40	9.37
Research compound[a]	4.184	8.67	8.55
Research compound[a]	4.332	5.60	5.46
5-Chloro-4-hydroxy-3-methoxybenzylisothiuronium phosphate	4.410	8.99	9.18

[a] Samples containing 30–45% fluorine.

In general, α-picoline seems to share all the advantages that quinoline possesses over ammonia and other bases as a precipitant for phosphomolybdate, and has additional benefits in that larger amounts of arsenate, silicate and citric acid can be tolerated without interference, and that the convenient single reagent solution is more stable. The fact that the precipitate cannot be weighed is only a marginal disadvantage, for the titration end-point is perfectly easy to see.

EXPERIMENTAL

Reagent solution

Dissolve 150 g of A.R. molybdenum trioxide and 30 g of A.R. sodium hydroxide in 500 ml of water by heating for about 30 min. Filter and add 400 ml of A.R. concentrated hydrochloric acid and 2–3 drops of 100-vol. hydrogen peroxide to remove the greenish-blue colour. Dissolve 22 ml of distilled α-picoline in 600 ml of 1:1 hydrochloric acid. Mix the 2 solutions, boil briefly, leave overnight and filter into a polythene bottle.

Procedure

Use an amount of orthophosphate corresponding to 0.2–1 mg of phosphorus and dilute the solution to *ca.* 20 ml. Heat to 90–100° and add 5 ml of the reagent solution in a fairly rapid stream with constant stirring. Boil briefly and allow to cool for a few minutes. As in the case of quinoline, the time of standing is unimportant. Filter the precipitate on a paper pulp pad and wash the flask twice with 5-ml portions of 1 *N* hydrochloric acid. Then rinse the flask, precipitate and filter with water until the washings are neutral to litmus. Transfer the pad and precipitate to a glass-stoppered flask, add an excess of standard 0.05 *M* sodium hydroxide and shake to dissolve. Back-titrate with standard 0.05 or 0.025 *M* hydrochloric acid using phenolphthalein as indicator.

Procedure for organic compounds

Decompose a sample of 3–6 mg by the oxygen-flask method described previously, absorbing the combustion products in 5 ml of 0.5 *M* sodium hydroxide and 4 ml of saturated aqueous bromine solution. After absorption is complete, rinse the gauze, etc., with 5 ml of water and 2.5 ml of *ca.* 1 *M* hydrochloric acid and boil gently to remove most of the bromine. Add 200 mg of citric acid (or up to 700 mg if necessary) and precipitate the α-picoline phosphomolybdate as described above. The rinsing with 1 *M* hydrochloric acid can be omitted when the solution contains citric acid.

Blanks should be determined in exactly the same way without an organic sample.

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SUMMARY

A selection of organic nitrogen bases was examined for the precipitation of phosphomolybdate. α-Picoline (2-methylpyridine) proved superior to the well-established quinoline; it is slightly more sensitive for phosphate, much less sensitive to arsenate and silicate, and less affected by citric acid so that phosphate can readily be determined in presence of these ions. The reagent solution is stable for at least a month. The α-picoline phosphomolybdate could not be used gravimetrically but the conventional titrimetric finish was satisfactory. The method was applied to the microanalysis of organic compounds.

RÉSUMÉ

Un choix de bases azotées organiques est examiné pour la précipitation du phosphomolybdate. L'α-picoline (méthyl-2-pyridine) se montre supérieure à la quinoléine. Ce réactif est légèrement moins sensible pour les phosphates, mais beaucoup moins pour arséniate et silicate; ce qui permet de doser les phosphates en présence de ces ions, de même qu'en présence d'acide citrique. Ce réactif est stable pendant un mois au moins. Le phosphomolybdate d'α-picoline ne peut pas être dosé gravimétriquement; on procède au dosage titrimétrique conventionnel. Cette méthode peut être appliquée à la microanalyse de composés organiques.

ZUSAMMENFASSUNG

Eine Auswahl organischer Stickstoffbasen wurde in Hinsicht auf die Fällung des Phosphormolybdats geprüft. α-Picolin (2-Methylpyridin) zeigte sich dem bewährten Chinolin überlegen. Es ist etwas empfindlicher für das Phosphat und sehr viel weniger empfindlich für Arsenat und Silikat und wird weniger durch Zitronensäure beeinflusst, so dass Phosphat in Gegenwart dieser Ionen leicht bestimmt werden kann. Die Reagenzlösung ist mindestens einen Monat lang stabil. Das α-Picolin-Phosphormolybdat konnte gravimetrisch nicht verwendet werden, jedoch war die konventionelle, massanalytische Methode befriedigend. Die Methode wurde für die Mikroanalyse organischer Verbindungen angewendet.

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SHORT COMMUNICATIONS

A rapid empirical method for the simultaneous determination of ammonium, fluorine and zirconium in ammonium hexafluorozirconate solutions

The reprocessing of irradiated reactor fuel elements using chemical decladding proceeds in 2 steps, namely the dissolution of the fuel element cladding, followed by the dissolution of the uranium fuel core. Fuel elements clad in zircaloy-2, a zirconium alloy containing 1.5% tin, are declad by means of a concentrated ammonium fluoride solution containing ammonium nitrate. The final solution is about 0.8 *M* in ammonium fluoride and 0.8 *M* in ammonium hexafluorozirconate. The ammonium, fluorine and zirconium concentrations have to be determined for control of the chemical process. The analyses must be carried out by remote control in lead-shielded air-tight boxes to cope with the radiation exposure hazard.

A method is described in this paper, for the simultaneous determination of the 3 constituents by potentiometric titration with sodium hydroxide solution. A recording titrator is used with a glass indicating electrode. The amounts of base corresponding to relevant points of inflexion on the titration curve and the slopes of the curve near these points are empirically related to the concentration of the 3 constituents.

Reagents

A standard ammonium hexafluorozirconate solution was prepared by dissolving a known amount of zircaloy in standard hydrofluoric acid in the presence of ammonium nitrate and adjusting the solution to pH 5.5 with ammonia. The tin present in the alloy dissolved as fluorostannate. The ammonium content of the solution was determined from the distillate after the ammonia had been separated by distillation.

A standard ammonium fluoride solution was prepared; the ammonium concentration was determined by acidimetric titration after addition of formaldehyde[1], and the fluoride concentration by compleximetric titration of calcium after addition of excess calcium ions and precipitation of calcium fluoride[2].

Procedure

Aliquots of the ammonium hexafluorozirconate and the ammonium fluoride solutions were added to the titration vessel and diluted to a volume of 50 ml. The approximate compositions of the 27 mixtures prepared, expressed as mg-atoms of zirconium and fluorine and mg-ions of ammonium present, are shown in Table I.

TABLE I

COMPOSITION OF THE EXPERIMENTAL SOLUTIONS

Zirconium (mg-atom)	*Fluorine (mg-atom)*	*Ammonium (mg-ion)*	*No. of solns.*
0.1	0.6–1.2	0.2–0.8	7
0.15	0.9–1.5	0.3–0.9	7
0.2	1.2–1.7	0.4–0.9	6
0.25	1.5–1.8	0.5–0.8	4
0.3	1.8–2.0	0.6–0.8	3

The solutions represent stable process solutions, in which the fluorine–zirconium ratio has been limited to avoid the precipitation of insoluble zirconium fluoride compounds.

The solutions were titrated against standard 0.500 N sodium hydroxide solution by means of a recording titrator (Metrohm E 336), which has a motor-driven syringe and which was connected to a combined glass–calomel electrode, Metrohm EA/121/UX. Stirring was required. The titrator records the derivative of the titration curve. The peaks in the record correspond to the relevant points of inflexion of the titration curve and the difference in height of two peaks is related to the difference in the slopes of the titration curve near these points.

A typical example of a titration curve is shown in Fig. 1. The reading of the first peak was improved by shifting it from the edge of the recorder chart. For this purpose a small amount of nitric acid was added to the titration vessel. The amounts of base added can be read to 0.005 meq and the difference in height to 0.05 cm.

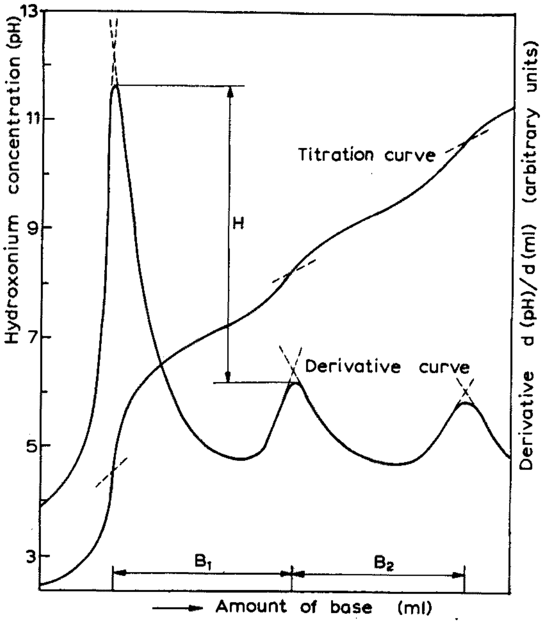

Fig. 1. A typical example of a recorded titration curve.

Results and discussion

The derivative titration curve shows 3 peaks. The amounts of base added up to the first peak, between the first and second peaks and between the second and third peaks correspond mainly to the neutralization of the hydroxonium ions present in the solution, the precipitation of the metal hydroxides, and the neutralization of the ammonium ions respectively. The fluoride concentration influences the position and the shape of the first and second peaks, and is related to their difference in height.

Linear regression analysis[3] of the 27 sets of data with the amount of zircaloy present in the titration vessel (Zr mg-atoms), the amount of base for hydroxide precipitation (B_1 meq) and the total amount of fluoride (F mg-atoms) as variables, yields the equation:

$$Zr = 0.01823 + 0.3588\ B_1 - 0.0542\ F$$

Analysis of the sets of data with the difference in height of the first and second peaks (H cm) as variable instead of the amount F gives the relationship:

$$Zr = 0.0273 + 0.2826\ B_1 - 0.00287\ H$$

The zircaloy concentration of an unknown sample can be determined by introducing into the relevant equation the experimentally found amount B_1 and the difference H of the amount F, determined independently. The coefficients of the equations are valid for the experimental conditions described and should be redetermined for each experimental arrangement. The error in a zircaloy determination can be estimated on the basis of the differences between the zircaloy amounts calculated by means of the equations and the true amounts. These residual values show a random distribution over the ranges of zirconium and fluorine concentrations investigated. The residual variances of the two regression equations are $4.4 \cdot 10^{-6}$ and $12.5 \cdot 10^{-6}$ respectively. The relative standard deviation of a single zircaloy determination by means of the second equation will be therefore 2–4 % depending on the amount in the titration vessel. The relationship between the amount of fluorine present in the titration vessel and the two measurable variables can be calculated accordingly, giving the equation:

$$F = -\ 0.149 + 0.053\ H + 1.406\ B_1$$

The residuals are randomly distributed. The residual variance is $27 \cdot 10^{-4}$, corresponding to a relative standard deviation between 3 and 8% for a fluorine determination in this way.

The amount of ammonium (NH_4 mg-ions) can be related to the amount of base for ammonium neutralization (B_2 meq) by the equation:

$$NH_4 = +\ 0.851\ B_2$$

The residual variance of the regression line is $1.5 \cdot 10^{-4}$. The relative standard deviation of the ammonium determination described is consequently 2–6 %.

Acidimetric titration with sodium hydroxide coupled with potentiometric indication can be used for the determination of many cation mixtures. The method described is easily adaptable for remote control, enables full use to be made of expensive laboratory space and gives a quick analysis which is sufficiently precise.

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2-Naphthyl-α-methoxyessigsäure als Reagenz für Natrium

In einer früheren Arbeit berichteten wir über die Darstellung der 2-Naphthyl-α-methoxyessigsäure und ihre Verwendung zur quantitativen Natriumbestimmung[1]. Es wurde gezeigt, dass man unter Einhaltung bestimmter Fällungsbedingungen Na^+ von anderen Alkalimetallionen in wässrig–methanolischer Lösung abtrennen kann. Da die Säure in Wasser wenig löslich ist, wurde ihr Kaliumsalz als Fällungsreagenz angewandt. Die bei dieser Methode noch vorhandenen Unbequemlichkeiten–Einhalten eines bestimmten Verhältnisses Wasser zu Methanol und Einschleppen von Kaliumionen in die Analyse–konnten nunmehr beseitigt werden. Wir untersuchten generell die Alkalimetallsalze der 2-Naphthyl-α-methoxyessigsäure und ihren Einfluss auf die Natriumbestimmung. Des weiteren wurden Störungen der Bestimmungsmethode durch andere Ionen erkannt und Möglichkeiten ihrer Ausschaltung angegeben.

Darstellung der 2-Naphthyl-α-methoxyessigsäure

Die Darstellung der Säure folgt einer von REEVE UND WOODS[2] gegebenen Vorschrift. Ausbeute, bezogen auf den Aldehyd, 43% der Theorie.

Darstellung der Alkalimetallsalze

Ausser Natrium bilden auch Li^+, K^+, Rb^+, Cs^+ mit der 2-Naphthyl-α-methoxyessigsäure Salze verschiedener Zusammensetzung. Die Alkalisalze der Säure werden durch Reaktion äquivalenter Mengen der entsprechenden Hydroxide mit der Säure dargestellt und kristallisieren bei nachfolgendem Einengen der Lösung aus. Zur Entfernung etwaiger Säurereste wurden die Salze mehrfach mit Äther gewaschen und anschliessend in der Trockenpistole bei 60° und 0.1 Torr getrocknet. Als Beweise für die angegebene Zusammensetzung wurden herangezogen: Titration der Säuregruppe in den sauren Salzen, C und H Bestimmung durch Elementaranalyse, flammenfotometrische Alkalimetallbestimmung.

Folgende Salze konnten erhalten werden:

		Neutral	*Einfach sauer*	*Zweifach sauer*
Li-salz	Schmp. (°)	289–290	224–225	—
Na-salz		298–300	242–243	—
K-salz		172–176	158–160	145–146
NH_4-salz		153–155	—	—
Rb-salz		197–199	213–215	—
Cs-salz		146–148	214–216	—

Als "neutral" sollen solche Salze bezeichnet werden, die im Molekül keine Säurefunktion sondern ein Alkalimetallkation enthalten. Als "einfach sauer" bzw. "zweifach sauer" sehen wir Salze an, die gemeinsam mit einem oder zwei Molekülen der Säure kristallisieren. Ob die einfach sauren Alkalimetallsalze als Doppelsalze anzusprechen sind, wird noch untersucht.

Die neutralen Lithium-, Natrium-, Rubidium- und Cäsiumsalze sind in Wasser leicht löslich, das Kalium- und Ammonium- sowie die sauren Kalium- und Cäsiumsalze sind etwas weniger gut löslich. Von dem sauren Natriumsalz, das zur analytischen Bestimmung des Na^+ herangezogen wird, lösen sich in Wasser von 20° 180 mg/100 ml, bei 0° 100 mg/100 ml; die Löslichkeit in einem Wasser–Methanol-Gemisch (3 Teile Wasser, 1 Teil Methanol) liegt bei 167 mg/100 ml bzw. 102 mg/100 ml[1].

Tetra-alkylammoniumsalze

Wie frühere Untersuchungen zeigten[1], ist der Unterschied der Löslichkeit des analytisch interessanten sauren Natriumsalzes in einem Wasser–Methanol-Gemisch (3:1) und reinem Wasser nur gering. Könnte man die Säure in eine wasserlösliche Verbindung überführen, vereinfachte sich die Fällung wesentlich, weil nicht mehr ein bestimmtes Wasser–Methanol-Verhältnis einzuhalten ist. Unter diesem Aspekt stellten wir das Tetramethylammonium- und das Tetraäthylammoniumsalz der 2-Naphthyl-α-methoxyessigsäure her. Beide Salze sind in Wasser sehr gut löslich, das erstere wird als Reagenz zur Natriumbestimmung vorgeschlagen.

Das Tetramethylammonium-2-naphthyl-α-methoxy-acetat ist ein farbloses, feinkristallines, hygroskopisches Pulver, das bei 177–179° schmilzt. Es ist in Substanz und in wässriger Lösung beständig. In neutraler Lösung findet keine Reaktion mit Natriumionen statt, deshalb wird in saurem Medium gearbeitet. Man kann sich vorstellen, dass die zum Ansäuern verwendete Salzsäure die 2-Naphthyl-α-methoxyessigsäure in Freiheit setzt, die sofort mit Natrium zum unlöslichen Natriumhydrogen-2-naphthyl-α-methoxy-acetat reagiert.

Herstellen der Reagenzlösung

129.7 g 2-Naphthyl-α-methoxyessigsäure (0.6 Mol) werden in einem 1-Liter-Masskolben mit 0.6 Mol Tetramethylammoniumhydroxid in Form der handelsüblichen 10-prozentigen Lösung unter Schütteln neutralisiert. Danach füllt man mit destilliertem Wasser bis zum Eichstrich auf. Diese Reagenzlösung ist monatelang beständig. Sollte etwas Kieselsäure ausfallen, wird vor Gebrauch filtriert.

Herstellen der Waschlösung

Als Waschflüssigkeit für den Niederschlag verwendet man Äthanol, das mit saurem Natriumsalz fast gesättigt ist. 270 ml handelsüblicher 96%iger Alkohol werden mit etwas Natriumhydrogen-2-naphthyl-α-methoxyacetat 4 Stunden gerührt, dann wird abfiltriert und auf 300 ml aufgefüllt. Für eine Analyse werden 50 ml dieser Lösung benötigt. Die Waschflüssigkeit kann unbeschränkte Zeit aufbewahrt werden.

Durchführen der Fällung

Die Konzentration des Na^+ in der Analysenlösung soll zweckmässigerweise zwischen 0.5 und 5 mg/ml betragen. Das Natriumsalz kann als Chlorid, Nitrat, Sulfat oder Perchlorat vorliegen. Die Analysenlösung wird mit 1 *N* Salzsäure angesäuert und auf einen pH-Wert zwischen 3 und 4 gebracht, indem man ihr pro ml verwendeten Reagenz 0.2 ml 1 *N* Salzsäure zufügt. Das Reagenz wird in 75%igem Überschuss zugegeben, um eine quantitative Ausfällung des Na^+ zu erreichen. Befinden sich z.B. 15–40 mg Na^+ in 20 ml Wasser, wird die neutrale Lösung mit 2 ml 1 *N* Salzsäure angesäuert und 10 ml Reagenz zugegeben. Die Fällung, die bei Raumtemperatur erfolgt, setzt sofort ein und ist nach 90–100 Minuten quantitativ. Nur bei sehr hohem Fremdionengehalt muss die Analyse länger stehen.

Der kristalline Niederschlag lässt sich gut abfiltrieren. Arbeiten bei 0° führt zu keiner Verbesserung der Methode. Der ausfallende Niederschlag ist hier feinkristallin und schwer filtrierbar, eine Verkürzung der Fällungszeit kann auch nicht erreicht werden.

Das Natriumhydrogen-2-naphthyl-α-methoxyacetat wird durch eine G4 Fritte abfiltriert. Man spült das Becherglas mit 5 ml Waschäthanol aus und wäscht den Niederschlag mit 3 mal 15 ml Waschlösung. Mit den ersten 5 ml Waschflüssigkeit wird bezweckt, dass das Natriumsalz von Wasser befreit wird und sich in den weiteren 45 ml keine grössere Natriumsalzmenge löst. Wie die Löslichkeitsuntersuchungen zeigen, ist die Löslichkeit des Natriumsalzes in Wasser–Alkohol-Gemischen grösser als in reinem Alkohol. Mit 5 ml Waschäthanol wird aber ein sehr günstiges Wasser–Alkohol-Verhältnis erreicht, so dass keine grösseren Fehler entstehen.

Das Natriumsalz bildet keine Hydrate. Der Niederschlag wird im Trockenschrank bei 105–110° eine Stunde getrocknet und ausgewogen. Faktor $f = 0.05059$.

Im ausgefallenen Natriumsalz $C_{10}H_7CH(OCH_3)COONa \cdot C_{10}H_7CH(OCH_3)$-$COOH$ ist die Carboxylgruppe titrierbar. Die Menge des Niederschlages und damit der Natriumgehalt kann also schnell und einfach durch Titration ermittelt werden. Dazu kocht man den Niederschlag in 250 ml destilliertem Wasser auf und titriert nach dem Abkühlen mit $N/10$ Natronlauge gegen Thymolblau als Indikator. Nach Abzug des Blindwertes werden die verbrauchten ml NaOH mit dem Faktor $f = 2.2991$ multipliziert und der Natriumgehalt in mg erhalten. Der Fehler der Methode beträgt ±1%. Die Fehlergrenze übersteigt auch bei Gesamtanalysen nicht 1%. Eine Anzahl Beleganalysen sind in den Literatur[3] angegeben.

TABELLE I

ANALYSEN

Eingewogene Menge (mg)	*Na berechnet (mg)*	*Na gefunden (mg)*	*Fehler (%)*
54.41 NaCl	21.4	21.6	+1.0
135.20 $NaClO_4$	25.4	25.2	−0.8
114.02 $NaNO_3$	30.8	31.0	+0.6
109.88 Na_2SO_4	35.6	35.2	−1.0
22.55 NaCl			
48.30 $NaClO_4$	36.3	36.5	+0.6
39.10 Na_2SO_4			
21.18 $NaNO_3$			
69.20 NaCl			
259.80 NH_4Cl	27.1	27.2	+0.4
61.02 NaCl			
298.23 LiCl	24.1	24.3	+0.8
109.20 $NaNO_3$			
500.84 KCl	29.5	29.8	+1.0
83.30 $NaNO_3$			
441.90 RbCl	22.5	22.4	−0.4
210.52 Na_2SO_4			
291.18 CsBr	68.1	68.0	−0.1
99.50 NaCl			
134.75 $MgCl_2$	39.1	38.7	−1.0

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Chemical separation and determination of small quantities of strontium and calcium

Chemical separation and determination of small quantities of strontium from calcium by WILLARD's nitrate method[1] has its limitations: calcium nitrate invariably coprecipitates, particularly when the nitric acid concentration is above 80%, and precipitation is incomplete when the amount of strontium is less than 60 mg. To overcome these difficulties, a new method of separation based on the precipitation of strontium on ignited barium sulphate from an alcoholic aqueous solution was investigated. Compleximetric titrations of the supernatant solution containing the separated calcium, and of the eluate containing the separated strontium fraction, allow a complete analysis for both the components of the mixture.

The efficiency of the separation procedure was checked by testing for strontium in the separated calcium fraction, and for calcium in the strontium-bearing barium sulphate carrier. For calcium, the radioactive isotope, calcium-45 was used as tracer[2], and for strontium, a concentrated and neutralized portion of the supernate was tested with sodium rhodizonate[3].

The optimum experimental conditions, ensuring quantitative uptake of strontium by the barium sulphate carrier and complete absence of calcium in the solid phase, were worked out by a systematic study of the influence, under otherwise identical conditions, of the significant factors.

The results showed that for quantitative separation the optimum conditions were: (*a*) alcohol concentration between 13 and 18%; (*b*) hydrochloric acid concentration between 0.1 N and 0.2 N; (*c*) potassium sulphate concentration between $5 \cdot 10^{-2}$ M and $8 \cdot 10^{-2}$ M; (*d*) barium sulphate carrier $\geqslant$300 mg and (*e*) quantity of strontium $\leqslant$ 3 mg. Calcium contents varying between 0.5 and 12 mg had no influence.

Reagents

All reagents used were of AnalaR grade. A 0.01 M magnesium chloride solution and 0.05 M EDTA solution were used for the final determination with a microburette graduated to 0.01 ml.

Procedures

Separation method. A typical separation is described. Take 300 mg of ignited barium sulphate in a 50-ml clean and dry centrifuge tube and to this add, in the following order (*i*) 5 ml of solution containing strontium (3 mg) and calcium (4 mg); (*ii*) 15 ml of aqueous ethanol (4 ml ethanol diluted to 15 ml with water); (*iii*) 5 ml of 0.75 *N* hydrochloric acid solution containing 285 mg of potassium sulphate. Stir the resultant suspension and allow to stand, stirring again twice, for 15–20 min. Centrifuge the suspension and wash the strontium-bearing carrier 3 times with 6-ml portions of wash solution (100 ml of wash solution contains 16 ml of ethanol, 20 ml of 0.75 *N* hydrochloric acid and 64 ml of 0.1 *M* potassium sulphate). Collect the supernate and washings in a titration flask. Finally, wash the carrier 3 times with 6-ml portions of 0.5 *N* hydrochloric acid. Collect the 3 leached solutions in a separate titration flask.

Radiochemical test for calcium in the strontium fraction. The strontium-bearing barium sulphate carrier was mixed to a slurry with acetone and transferred to a clean dry planchet with a dropper, after which it was dried by infrared heating. The activity was measured with an end-window G.M. counter in conjunction with a decatron scaler. Corrections for the background count-rate were made; decay and dead-time corrections were insignificant.

Determination of strontium and calcium. Add two drops of methyl orange to the strontium fraction eluted from the carrier. After neutralizing with concentrated ammonia solution, add appropriate amounts of ammoniacal buffer solution and eriochrome black T indicator and a known excess of standard EDTA solution; back-titrate with magnesium chloride solution, observing the colour change under a tungsten filament lamp[4].

The possible interference in the compleximetric determination of strontium by passage of traces of barium into the eluate was examined carefully. Ignited barium sulphate was washed 3 times with 6-ml portions of 0.5 *N* hydrochloric acid solution and the total leached solution was evaporated to dryness; an examination of the residue by the flame colour showed the absence of barium.

TABLE I

DETERMINATION OF STRONTIUM AND CALCIUM IN MIXTURES

(K_2SO_4 concn. $6.5 \cdot 10^{-2}$ *M*; HCl concn. $15 \cdot 10^{-2}$ *M*; amount of carrier (ignited $BaSO_4$) 300 mg; 16% ethanol in aqueous medium)

Composition of mixture taken		*Amounts found in supernate*[a]		*Amounts found in the eluate*[a]	
Ca (mg)	*Sr (mg)*	*Ca (mg)*	*Sr (mg)*	*Ca (mg)*	*Sr (mg)*
0.5	3.0	0.508	0.0[b]	0.0[c]	2.991
1.0	3.0	1.004	0.0[b]	0.0[c]	2.991
2.0	3.0	2.000	0.0[b]	0.0[c]	2.982
4.0	3.0	4.000	0.0[b]	0.0[c]	3.009
8.0	3.0	7.992	0.0[b]	0.0[c]	2.982
12.0	3.0	11.992	0.0[b]	0.0[c]	2.991
4.0	2.0	3.996	0.0[b]	0.0[c]	1.991
4.0	1.0	4.004	0.0[b]	0.0[c]	0.982

[a] Absence of barium ions was checked independently by the flame colour.

[b] Checked with sodium rhodizonate.

[c] Checked radiometrically.

The calcium fraction present in the separated supernate was determined, independently, by similar compleximetric titration.

Results and discussion

The results of analysis of a few typical mixtures (Table I) indicate the suitability of the procedure for mixtures involving small quantities. Separation of strontium by carrier-precipitation is limited by factors such as hydrogen ion, alcohol and sulphate ion concentrations. The method is also limited by the quantity of strontium (< 3 mg); larger quantities could possibly be separated by increasing the amount of barium sulphate carrier. The quantity of calcium, up to 12 mg, in the mixtures poses no problem in the separation, although the determination of small quantities of calcium (< 0.5 mg) in the supernate is subject to the normal limitations of EDTA titrations. An advantage of the procedure is that an analysis can be completed in 2 h. The method can be further simplified, if 0.15 N sulphuric acid is used as the precipitant instead of potassium sulphate–hydrochloric acid mixture. However, in order to study the influence of sulphate ions and hydrogen ions individually, the latter mixture was used throughout the investigation.

A possible mechanism for the separation may be suggested: the ionic lattice of ignited barium sulphate, though chemically inert, is prone to adsorb the lattice anions, namely the sulphate ions, which are deliberately kept in excess; a layer of the available cations, *i.e.* strontium and calcium, depending on the respective bulk concentration, then enter into the so-called counter ionic layer. Subsequent ionic interaction between the cationic and anionic species of the "double layer" ensures that ultimately the more insoluble strontium sulphate only is precipitated on the surface of barium sulphate. The preferential precipitation of strontium sulphate instead of calcium sulphate is decided by the lattice and solvation energies of the cations involved; alcohol of the specified concentration is undoubtedly important in effecting a selective precipitation.

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The determination of zinc by substoichiometric isotope dilution. A note.

In a recent paper[1] attention was drawn to the limitation imposed on the sensitivity of the substoichiometric determination of zinc[2,3] if the buffer-masking solution used contains dithizone. It was also stated that the non-stoichiometry of the zinc–dithizone reaction in the presence of oxalate ions must be taken into account.

In the original papers[2,3] it was perhaps not made sufficiently clear that the buffer-masking solution must be completely free from organic reagent, but the point was stressed in a later paper[4] in which the following sentences appear. "The last traces of organic reagents must be removed after the purification (of the buffer-masking solution by extraction with dithizone) is finished. This can be accomplished by successive extraction with chloroform followed by storage in light, during which any dithizone present in an aqueous solution rapidly decomposes." The purification of the buffer-masking solution is best done by extractive titration with very dilute solutions of dithizone, so that only very small amounts of dithizone are transferred to the aqueous phase.

With regard to the possible effect of oxalate[1], it appears from the stability constant of zinc oxalate that oxalate ions in the concentrations used will not decrease the percentage extraction of zinc at pH 8.5–9.0 although the time of extraction must be increased. However, in any case in substoichiometric analysis, the standard and test solutions are always treated in exactly the same way, *i.e.* in the presence of oxalate in this special case, and so inaccurate results cannot be caused by any influence of the complexing agent.

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Note sur la lactonisation de l'acide hydroxyéthylènediaminetriacétique. Mise en évidence par thermogravimétrie et spectrométrie infrarouge

Dans le cadre de nos recherches[1,2] sur la séparation sur échangeurs d'ions des lanthanides et des actinides par l'acide hydroxyéthylènediaminetriacétique (HEDTA), nous avons été amené à vérifier la pureté du complexant utilisé.

Alors que la littérature renseigne 159° comme température de fusion du HEDTA, il s'avère, qu'en réalité, cette température de 159° est le point de lactonisation de la substance. La fusion, suivie immédiatement d'une décomposition, se situe à la température de 215°.

Observation au microscope à plaque chauffante

A 159°, les cristaux paraissent brusquement fondre puis se ressolidifient et ne subissent plus aucun changement jusqu'à la température de 215°. A cette température, ils fondent franchement pour bientôt se décomposer.

Etude thermogravimétrique

Les résultats sont consignés dans le Tableau I. La perte de poids reste la même pour des durées de chauffage de 2, 3 ou 5 h. L'enregistrement de la courbe thermogravimétrique (Fig. 1) confirme ces résultats.

TABLEAU I

THERMOGRAVIMÉTRIE DE L'ACIDE HYDROXYÉTHYLÈNEDIAMINETRIACÉTIQUE

(60 min de chauffage à 162°)

Poids de l'échantillon (g)	*Poids après chauffage (g)*	*Perte (g)*	*Perte par môle de HEDTA (g)*
1.0144	0.9490	0.0654	17.92
3.0237	2.8284	0.1953	17.95
5.1823	4.8474	0.3351	17.98

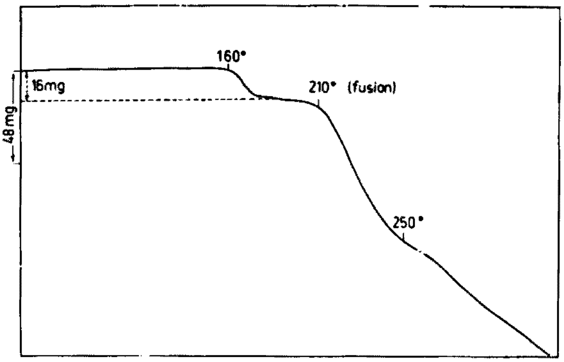
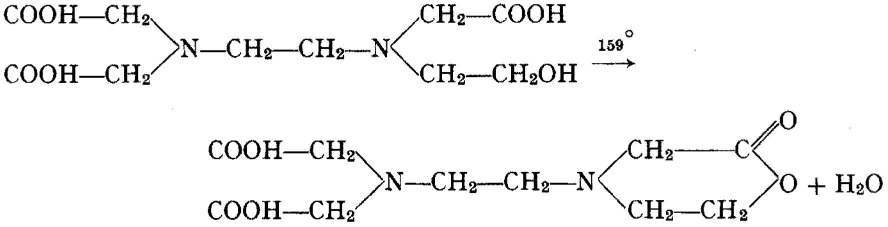


Fig. 1. L'enregistrement de la courbe thermogravimétrique de HEDTA. Programme: 150°/h; temperature 25 à 350°; poids 0.2493 g; p.m. 278.

Anal. Chim. Acta, 37 (1967) 542–545

Il est, d'autre part, établi que l'HEDTA cristallise sans molécule d'eau. La thermogravimétrie montre, cependant, que chauffé à une température supérieure à 159°, il perd une molécule d'eau. Il est alors logique d'admettre une réaction interne de déshydratation conduisant à la formation d'une lactone.



Cette hypothèse a été vérifiée par spectrométrie infrarouge.

Etude par spectrométrie infrarouge

Nous avons essayé de mettre en évidence par spectrométrie infrarouge la formation de la lactone vers 159°.

HEDTA sous ses 2 états (acide et lactone) ainsi que ses sels alcalins sont insolubles dans les solvants habituels de l'infrarouge; par contre, il est soluble dans la pyridine mais les bandes d'absorption du solvant gênent. La technique des pastilles de KBr ne convient pas non plus étant donné que, d'une part, HEDTA réagit plus ou moins profondément avec KBr pour donner le sel potassique et que, d'autre part, le cycle lactonique est également brisé avec formation du sel potassique. La seule méthode qui nous ait fourni des résultats est la suspension de la substance dans le perfluorokérosène.

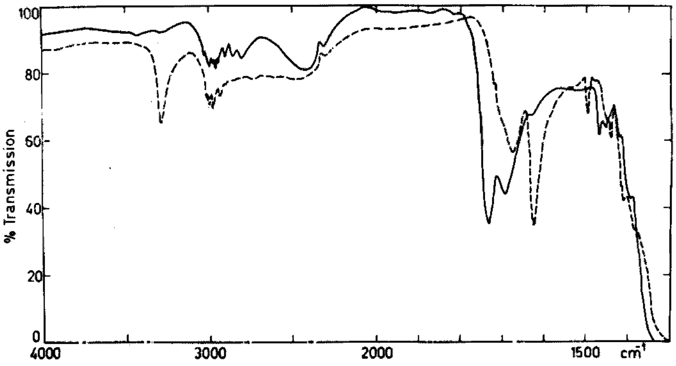
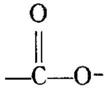


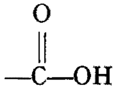
Fig. 2. Les spectres infrarouge de 4000 à 1400 cm^{-1}.

La Fig. 2 reproduit les spectres infrarouge de 4000 à 1400 cm^{-1} de HEDTA et de HEDTA ayant perdu une molécule d'eau.

Ces spectres ont été enregistrés au Perkin Elmer Mod. 125.

Le spectre du HEDTA non chauffé présente 4 régions d'absorption:

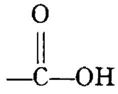
1625 cm⁻¹ = l'acide se trouvant sous forme de Zwitterion[3], on a affaire à une bande d'absorption du carbonyle  $-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$

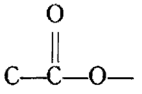
1675 cm⁻¹ = bande d'absorption du carbonyle[3]  $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

2900–3000 cm⁻¹ = vibrations de valence CH[3,4]

3290 cm⁻¹ = étant donné que cette bande ne disparaît pas dans le sel trisodique du HEDTA, il faut bien admettre qu'il s'agit de la vibration de valence du OH de la fonction alcool dans HEDTA.

Le spectre du produit qui a perdu une molécule d'eau par chauffage à 160° montre les bandes suivantes:

1695 cm⁻¹ = bande d'absorption du carbonyle du  $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

1730 cm⁻¹ = bande d'absorption de  $C-\overset{\overset{\displaystyle O}{\|}}{C}-O-$ lactonique[5]

2900–3000 cm⁻¹ = vibrations de valence CH[3,4].

Disparition de la bande OH à 3290 cm⁻¹ qui constitue la preuve la plus directe de la formation d'une lactone par départ d'une molécule d'eau à la température de 159°.

Mise en évidence chimique de la fonction lactonique

Nous avons utilisé la réaction d'identification des lactones décrite dans la littérature[6]: dans des conditions de température et de pH adéquates, l'hydroxylamine réagit avec les lactones et le produit formé réagit lui-même avec le chlorure ferrique pour donner un composé de couleur rouge-magenta caractéristique.

$$R{-}COO{-}R^1 + NH_2OH \rightarrow RCO(NHOH) + R^1OH$$

$$3\ R{-}CO(NHOH) + FeCl_3 \rightarrow RCO(NHO)_3Fe + 3\ HCl$$

Ce test est positif.

En conclusion, on peut affirmer sur la base des essais de thermogravimétrie, de spectrométrie infrarouge et de test chimique, que la température de fusion de HEDTA renseignée dans la littérature (159°) correspond, en fait, à la température de lactonisation avec perte d'une molécule d'eau.

La température de fusion de la lactone formée est de 215°.

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The determination of boron in dilute aqueous solutions by neutron activation analysis

The determination of boron in waters, industrial wastes, and sewage effluents is important in agriculture. In minute quantities, boron is essential to plant life, but larger amounts are toxic to plants and may cause soil sterilization. Of growing concern is the increase in the boron content of some waters due to the use of fire-retardant chemicals such as sodium calcium borate[1]. Boron in excess of 2 mg/l in irrigation water is deleterious to many plants, and there is evidence[2] that some are adversely affected by as little as 1 mg/l.

The analysis of boron in aqueous solutions is also assuming greater importance in nuclear technology with the recent adoption of the chemical shim as a means of providing excess $\Delta k/k$ in nuclear reactors[3,4]. A soluble chemical shim material (neutron poison) is added to the moderator or primary system; this method of control offers significant advantages and is being evaluated extensively. Boric acid has been selected as one of the more desirable chemical shim agents[5]; sufficient natural reagent-grade boric acid is usually added to elevate the moderator boron concentration to about 10 p.p.m. During the boric acid injection, the boron concentration in the moderator is monitored continuously to check any decrease in concentration that would indicate gross boron deposition on the moderator system surfaces.

In 1955 WANKE AND MONSE illustrated the use of the (n, α) reaction for the determination of boron[6]. Thin, solid samples were placed on fine sulfide phosphors which were used to detect the emitted α-particles. FITI *et al.*[7] used a similar technique in the analysis of minerals. A gas proportional counter was used by CLARK AND RASMUSSEN[8] to detect the charged particles resulting from the (n, α) reaction; in their work the chamber walls were made from the sample to be analyzed. ISENHOUR AND MORRISON[9] employed a NaI(Tl) scintillation detector to detect the γ-rays emitted by the excited lithium-7 daughter nucleus when solid samples containing boron were irradiated.

The present paper describes a method for the determination of boron in aqueous solutions by observing the (n, α) reaction on boron-10 when the solutions are homogeneously mixed with liquid organic phosphors and placed in a thermal-neutron flux.

Experiments with a plutonium–beryllium neutron source imbedded in a paraffin block showed that liquid scintillation pulses due to the recoiling (n, α) reaction products can be detected in the solution above a background of γ-ray and recoil proton pulses.

This method takes advantage of the fact that at least a major fraction of the energy of the (n, α) reaction on boron is imparted to the lithium-7 and helium-4 product nuclei as kinetic energy. In approximately 92% of these reactions nearly 0.5 MeV of energy is retained as internal excitation by the lithium-7 nucleus[9]. The excited lithium state is unstable and possesses a lifetime of $7.7 \cdot 10^{-14}$ sec; transition to the ground state involves emission of a γ-ray with an energy of 0.477 MeV. The boron-containing solution is mixed with a miscible liquid scintillating solution in a quartz vial which is optically coupled to an electron multiplier phototube. In a neutron flux, the liquid phosphor is excited by the recoiling helium and lithium nuclei, and the fluorescent light is measured by the phototube, the resultant pulses being stored in one of 256 channels of a multichannel pulse-height analyzer. A distance of approximately 4.5 cm between the plutonium–beryllium source and the sample gives a maximum signal from the sample.

Several recipes have been proposed for liquid phosphors which are appreciably miscible with aqueous solutions. Of those tried, the formulations proposed by KALLMAN *et al.*[10] and BRAY[11] proved most successful. BRAY's solution gave the highest light output at a volume concentration of 20% water. Americium-241 dissolved in a mixture of water and the phosphor was used to test the light output and to calibrate the analyzer. The analysis of several hundred thousand pulses from a boron-containing sample gave a spectrum with a peak at approximately 2.3 MeV, rising from a plateau caused by proton recoil, due to the fast neutron component in the neutron flux, and by γ-rays from the source or from (n, γ) capture reactions. A distilled water blank provides a reference spectrum which can be used to correct for the unwanted contribution due to proton recoil.

Procedure

The aqueous sample (3 ml) is added to the quartz vial along with 12 ml of BRAY's solution. The vial is optically sealed to the phototube with Dow-Corning silicone fluid, and the entire vial–phototube assembly is placed in the paraffin block 4.45 cm from a 1-c plutonium–beryllium neutron source. The paraffin block is surrounded by a light tight box (Fig. 1). The photomultiplier tube is fitted with a high-voltage divider

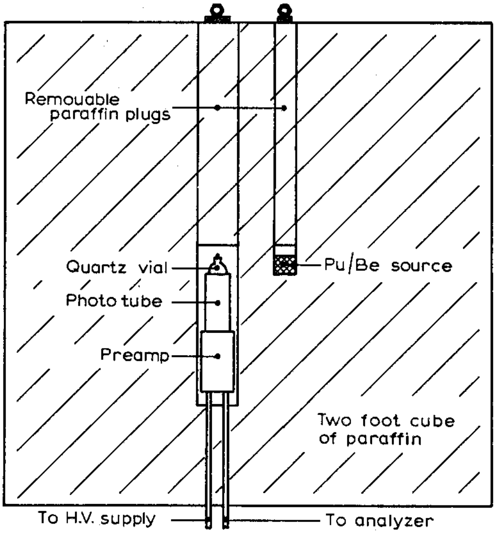

Fig. 1. Cross section view of paraffin moderator containing detector and source.

network and a cathode-follower preamplifier which supplies output pulse characteristics suitable for acceptance by the multichannel analyzer.

Pulses are analyzed for 20 min and the resulting spectrum is recorded on punched paper tape. A spectrum of a triple-distilled water blank is subtracted from the sample spectrum. The counts in the several channels under the 2.3-MeV boron peak are summed to obtain a measure of the boron concentration. Figure 2 shows a typical set of spectra for a boron-containing solution, a distilled water blank and the resultant difference spectrum.

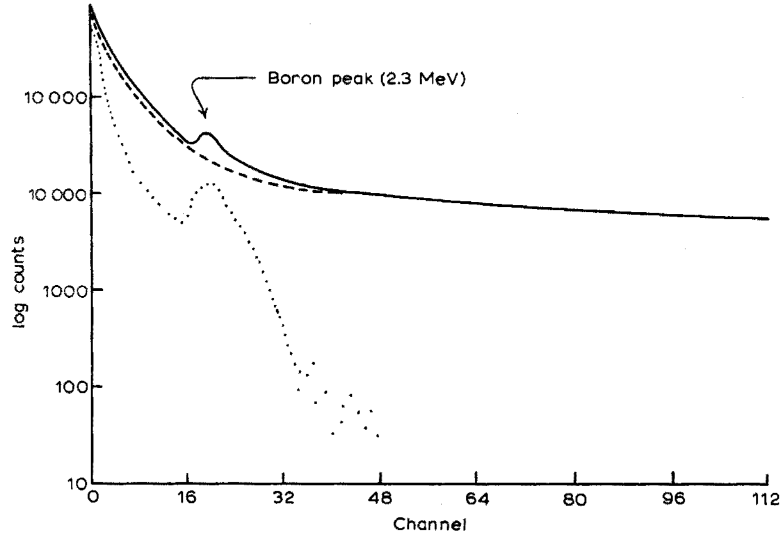

Fig. 2. Pulse height spectra of typical boron solution, distilled water blank and resultant net curve. — Sample; ---- Blank; ······ Sample minus blank.

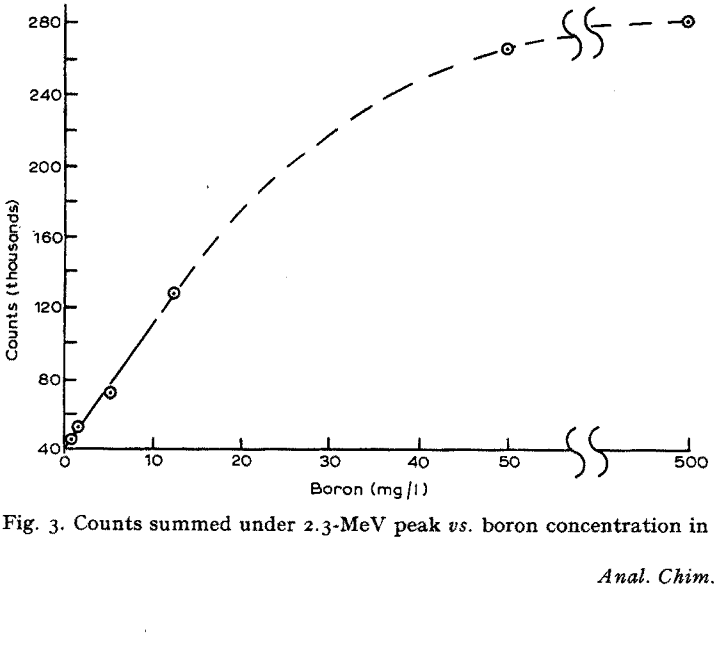

Fig. 3. Counts summed under 2.3-MeV peak *vs.* boron concentration in aqueous solution.

Discussion

A series of solutions made up with known boron concentrations was analyzed by this procedure. The total counts under each boron peak were plotted to yield the curve shown in Fig. 3. The levelling-off of counts at higher concentrations signifies absorption of a major fraction of the neutrons by outer layers of the solution. A plot of counts *vs.* boron concentration in the more dilute solutions showed the expected linearity. These results indicate that it is possible to analyze boron in the range 1–10 mg/l using a 1-c Pu–Be source, a 2-foot cube of paraffin, a photomultiplier and a multichannel pulse-height analyzer. This apparatus was originally conceived as a portable field instrument for surveying boron concentrations in natural waters. Since the Pu–Be source requires no power and relatively light shielding and since transistorized, battery-operated analyzers are readily available, this application appears quite feasible.

Further work in this laboratory is directed towards increasing the sensitivity of the method by utilizing a more highly thermalized beam from a nuclear reactor to reduce the interference due to proton recoil. A coincidence technique might eliminate extraneous pulses from various impurities by counting only those phosphor recoil pulses which are accompanied by the 0.477-MeV γ-ray from the lithium-7 daughter nucleus.

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BOOK REVIEWS

R. W. MOSHIER AND R. E. SIEVERS, *Gas Chromatography of Metal Chelates*, International Series of Monographs in Analytical Chemistry, Vol. 23, Pergamon Press, Oxford, 1966, viii + 163 pp., price 35 s.

This is a small but very useful book on the gas chromatographic separation and estimation of metal chelates. It is subdivided into 5 excellently written subsections concerning such aspects as instrumentation and techniques, analytical determinations and applications of gas chromatography in studies of metal complexes. The sections on instrumentation and analytical determination are well organised and to any beginner in this field will be most useful, covering in detail the chromatographic conditions, such as column temperature, gas flow-rate, detection system, recorder sensitivity and other essential data for successful application of the method. The final chapter of the book covers applications of gas chromatography to the metal chelates, including the resolution of optical and geometric isomers and its application to kinetic studies.

Each subsection is supported by an excellent reference system and the book will make a most useful addition to the library of any department interested in metal chelates.

J. THOMSON (London)

Anal. Chim. Acta, 37 (1967) 549

Handbook of Physical Constants, Edited by S. P. CLARK, JR., Revised Edn., Memoir 97 of the Geological Society of America, Geological Society of America Inc., New York, 1966, vii + 587 pp., price $ 8.75.

This volume is a completely revised and much expanded edition of a compilation of the same title first published in 1942 and reprinted several times. It has been the editor's aim to gather into it a wide variety of physical data useful for geological and geophysical calculations, and in this purpose he has been very successful. The book is divided into 27 sections compiled by specialist authors. The data have been critically selected, but few references to literature later than 1961 are cited. Although many of the sections will be of use principally to geophysicists, geochemists will find much to interest them, in particular the following sections: Composition of rocks (S. P. CLARK), Abundances of the elements (A. G. W. CAMERON), Isotopic abundances and 1961 atomic weights (S. P. CLARK), Melting and transformation points in oxide and silicate systems at low pressure (F. C. CRACEK AND S. P. CLARK), Phase relations in sulphide systems (G. KULLERUD), High pressure phase equilibria (S. P. CLARK), Pressure–volume–temperature and phase relations of water and carbon dioxide (G. C. KENNEDY AND W. T. HOLSER), Binary mixtures of volatile components (H. J. GREENWOOD AND H. L. BARNES), Ionization constants in aqueous solutions (H. L. BARNES AND H. C. HELGESON), Solubility (S. P. CLARK), Radioactive decay constants and energies (G. W. WEATHERILL), Abundances of uranium, thorium and potassium (S. P. CLARK, Z. E. PETERMAN AND K. S. HEIER).

J. P. RILEY (Liverpool)

Anal. Chim. Acta, 37 (1967) 549

ANNOUNCEMENTS

MEETINGS OF THE GESELLSCHAFT DEUTSCHER CHEMIKER 1967

April 17–21, 1967. Euchem-Conference on The Nature of the Hydrogen Bond, Schloss Elmau. (On special invitation only)

May 9–11, 1967. Symposium on Analysis and Chemistry in the Molten State, Freudenstadt. (organized by the Analytical Chemical Division of the GDCh)

June 27, 1967. Festive Meeting of the Gesellschaft Deutscher Chemiker on the occasion of the ACHEMA 1967 in Frankfurt (M).

August 28–September 1, 1967. 3rd International Symposium on Metalorganic Chemistry, München.

September 18–23, 1967. General Assembly of the GDCh and Centennial of the German Chemical Society, Berlin.

The following Divisions will have special meetings on the occasion of the General Assembly of the GDCh: *Analytical Chemistry Division* (Structure Analysis of Organic Compounds); *Applied Electrochemistry Division* (Organic Electrochemistry); *Pigments and Dyes Division*; *History of Chemistry Division*; *Industrial Judicial Protection Division*; *Nuclear-, Radio- and Radiation Chemistry Division* (Preparation and Chemistry of the Transuranium Elements); *Polymers and Plastics Division*; *Food Chemistry and Forensic Chemistry Division*; *Water Chemistry.*

September 25–29, 1967. International Mass Spectrometry Conference, Berlin. (organized by the Analytical Chemistry Division of the GDCh, sponsored by A.S.T.M.-E14 (USA), A.G. Massenspektroskopie der D.P.G. (Germany), G.A.M.S. (France), Institute of Petroleum-H.R.G. (Great Britain))

October 10–13, 1967. 4th International Symposium on Separation Methods with Special Consideration of Chromatography, Heidelberg. (organized by the Analytical Chemistry Division and the G.A.M.S.)

Details concerning the above-mentioned events may be obtained from: Gesellschaft Deutscher Chemiker, 6000 Frankfurt (Main), Postfach 9075, Deutschland.

AMERICAN CHEMICAL SOCIETY—ANALYTICAL DIVISION. ANALYTICAL SUMMER SYMPOSIUM

The 1967 Analytical Summer Symposium will be devoted to "Modern Titrimetry". The event, which is jointly sponsored by the Analytical Division of ACS and by the journal *Analytical Chemistry*, is scheduled for June 21–23, 1967, at Pomona College, Claremont, Calif. The program will feature several papers on specific ion electrodes and a round table discussion led by experts active in this field. Other topics will include new end-point determinative techniques and novel developments in electrochemical and thermochemical titrations in aqueous and non-aqueous solvents. Talks will be spaced at 1-h intervals, in order to allow ample time for presentations in depth and discussion. Further information about the program may be obtained from JOSEPH JORDAN (212 Whitmore Laboratory, Pennsylvania State University, University Park, Pa. 16802). Inquires concerning local arrangements should be directed to ALVIN L. BEILBY (Department of Chemistry, Pomona College, Claremont, Calif. 91713).

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This 7th edition has involved complete revision and reorganisation of the subject in order to present a still clearer picture of the multitudinous applications open t[illegible]rganic spot test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot test techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis*) and by limiting the number of tables and structural formulae.
Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
Functional group tests	70	109
Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
Differentiation of isomers etc.	0	54
Applications in the testing of materials etc.	111	131

In total the book now gives in 561 sections information on more than 900 tests compared with 600 tests in 346 sections in the preceding edition.

An important feature is the inclusion of a large number of recently developed tests and comments which have not hitherto been published in any form.

It is the author's hope that this work will help to correct the widespread impression that physical instrumentation is always superior to chemical methods for solving analytical problems. Each of the chapters presents instances of problems for which no solutions by physical means have yet been developed, or for which the rapid spot tests are equal or superior to the expensive instrumental procedure.

CONTENTS: 1. Development, present state and prospects of organic spot test analysis. 2. Preliminary (exploratory) tests. 3. Detection of characteristic functional groups in organic compounds. 4. Detection of structures and certain types of organic compounds. 5. Identification of individual organic compounds. 6. Application of spot tests in the differentiation of isomers and homologous compounds. Determination of constitutions. 7. Application of spot reactions in the testing of materials, examinations of purity, characterization of pharmaceutical products, etc... Appendix: Individual compounds and products examined. Author index. Subject index.

FROM REVIEWS OF THE SIXTH EDITION

... This new book, like its author, is unquestionably a giant on the analytical scene...
Journal of the Royal Institute of Chemistry

... Die Tatsache, dass Feigls klassisch gewordenes Werk, welches überall mit Begeisterung aufgenommen wurde, bereits in 6. Auflage erscheint, ist an sich Empfehlung genug... Es ist also eine wahre Fundgrube für neue Experimentaluntersuchungen... *Chimia*

... Even in these days of physical instrumentation there is ample room for the techniques described in this book which were originated and largely developed by Prof. Feigl. They are mostly very quick and very economical on materials. They sometimes present solutions to problems so far insoluble by expensive physical methods...
Laboratory Practice

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