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Vol. **44**, No. **1**	January 1969	
Vol. **44**, No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45**, No. **1**	March 1969	
Vol. **45**, No. **2**	April 1969	
Vol. **45**, No. **3**	May 1969	**(completing Vol. 45)**
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Vol. **46**, No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47**, No. **1**	August 1969	
Vol. **47**, No. **2**	September 1969	
Vol. **47**, No. **3**	October 1969	**(completing Vol. 47)**
Vol. **48**, No. **1**	November 1969	
Vol. **48**, No. **2**	December 1969	**(completing Vol. 48)**

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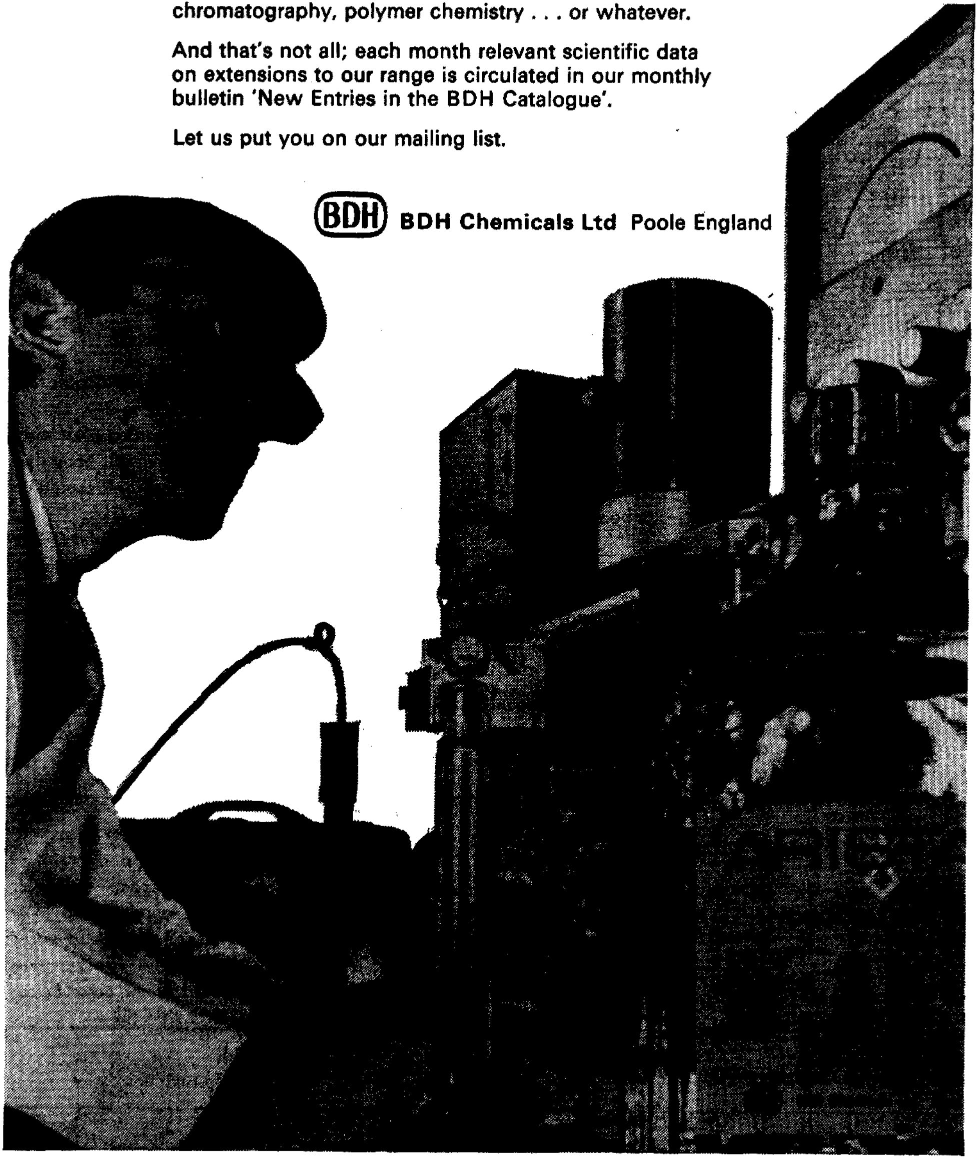

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NUCLEAR DESALINATION

Proceedings of a Symposium on Nuclear Desalination held by the International Atomic Energy Agency in Madrid, 18-22 November 1968

Published for the International Atomic Energy Agency, Vienna, Austria

6½ x 9½", xvi + 941 pages, 302 illus., 1969, Dfl. 110.00
SBN 444-40806-1

Water supply planners are looking more and more to desalination as a means by which supplemental and new water supplies can be offered at acceptable cost in those regions where natural water supplies are becoming fully utilized. There the water demands are relatively large, nuclear reactors can be an economic energy source for a desalination plant, especially when desalination is combined with the production of electricity in dual-purpose and multi-purpose plants.

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Nearly 300 participants from 36 countries and international organizations discussed more than 60 papers on desalination and reactor applications, research, recent developments and studies, and large desalination plant operating experience. Papers also described agro-industrial complexes and the potential that the energy centre concept may hold for integrated and large-scale area development in certain underdeveloped regions. This concept is of special interest to those countries which are now major importers of food and fertilizers; which possess raw materials that can be processed by energy-intensive industries; or which have climates favourable to year-round agriculture and fertile but 'under-watered' soils.

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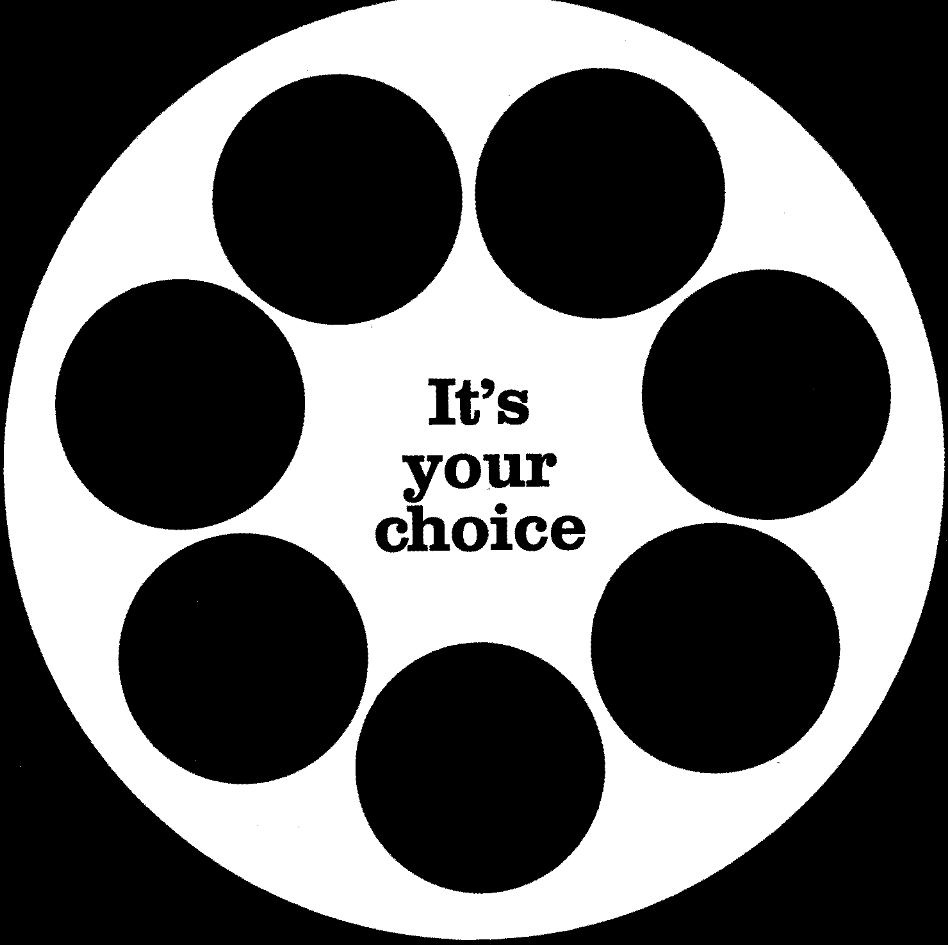
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 47, No. 3, October 1969

NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART V. SIMULTANEOUS DETERMINATION OF METALLIC IMPURITIES

Neutron activation analyses for Na, K, Cr, Fe, Co, Cu, Zn, Ga, Ag, Cd, La, W, Au and Tl in high-purity selenium in the p.p.m. and p.p.b. ranges were performed by irradiating 100-mg samples together with standards at a flux of 10^{13} n cm^{-2} sec^{-1}. The matrix activities from selenium, arsenic, germanium and bromine isotopes were separated by distillation in sulphuric acid–hydrobromic acid at 200–220°. The γ-emitting isotopes were measured simultaneously by γ-spectrometry with a Ge(Li) detector. The pure β-emitter ^{204}Tl was precipitated as tetrathiourea thallium(I) perchlorate and thallium(I) chromate and counted with a G.M.-tube.

C. BALLAUX, R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 47 (1969) 397–405

THE DETERMINATION OF SILICON BY FLAME PHOTOMETRY AND ATOMIC FLUORESCENCE SPECTROSCOPY WITH A SEPARATED NITROUS OXIDE–ACETYLENE FLAME

The flame photometry and atomic fluorescence spectroscopy of silicon in nitrogen and argon separated nitrous oxide–acetylene flames have been investigated. The high-temperature, reducing, fuel-rich, argon-separated flame permits the detection of down to 5 and 0.55 p.p.m. of silicon in aqueous solution by flame photometry and atomic fluorescence, respectively. A silicon microwave-excited electrodeless discharge tube was prepared and used for excitation of the atomic fluorescence. The optimum conditions for the determination of silicon by both techniques have been investigated. The fluorescence technique showed no interference from hundred-fold amounts (relative to silicon) of 23 ions, but 5 ions interfered in the determination by flame photometry. The fluorescence technique was also largely free from quenching and scatter effects in the presence of these extraneous ions.

R. M. DAGNALL, G. F. KIRKBRIGHT, T. S. WEST AND R. WOOD,
Anal. Chim. Acta, 47 (1969) 407–413

USE OF INTEGRATION READOUT TECHNIQUES FOR LOW ABSORBANCE SAMPLES IN ATOMIC ABSORPTION SPECTROSCOPY

An analog integrator is described and evaluated for the application of integrator techniques to low absorbing solutions by atomic absorption spectroscopy. Use of solid state operational amplifiers allows a stable, low drift integration of information signals to improve signal-to-noise ratios. The effects of experimental parameters are described and integration working curves are shown for solutions absorbing with 0–4% range.

W. W. HARRISON AND F. E. BERRY,
Anal. Chim. Acta, 47 (1969) 415–423

RADIOCHEMICAL SEPARATION OF GALLIUM BY AMALGAM EXCHANGE

An amalgam-exchange separation of radioactive gallium from a number of interfering radioisotopes has been developed. A dilute (*ca.* 0.3%) gallium amalgam is agitated with a slightly acid solution of $^{72}Ga^{3+}$ containing concentrations of sodium thiocyanate and either perchlorate or chloride. The amalgam is then removed and the radioactive gallium stripped by agitation with dilute nitric acid. The combined exchange yield of the perchlorate–thiocyanate system is 90 ± 4% and that of the chloride–thiocyanate system is 75 ± 4%. Decontamination yields of most of the 11 interfering isotopes studied were less than 0.02%. The technique is applicable for use with activation analysis for the determination of trace amounts of gallium.

R. R. RUCH,
Anal. Chim. Acta, 47 (1969) 425–429

THE X-RAY SPECTROMETRIC DETERMINATION OF URANIUM AND PLUTONIUM IN SOLUTIONS OF SPENT NUCLEAR FUELS

X-Ray spectrometry is applied to the determination of uranium and plutonium in dissolver solutions containing fission-product activities up to 1330 mCi. Uranium was measured in the concentration range 0.05–18 mg/g of solution and plutonium in the range 0.6–1.2 mg/g of solution with thorium as an internal standard. Plutonium was determined in the presence of a large excess of uranium and solutions with U/Pu ratios up to 300 were measured. The relative standard deviation of a single measurement was 1.0–3.0% over the concentration ranges investigated. The effect of direct γ-radiation from the sample on the detector background was demonstrated and minimized by means of lead shielding. It is suggested that samples with radioactivity levels up to 2 Ci could be measured safely and without seriously increasing the detector background. The application of this method at certain points in the nuclear fuel cycle may be important in the safeguarding of nuclear fuel.

P. A. PELLA AND A. v. BAECKMANN,
Anal. Chim. Acta, 47 (1969) 431–438

THE UTILISATION OF FUEL-RICH FLAMES AS SULPHUR DETECTORS

Hydrogen-rich flames are rapidly assuming an important role as highly sensitive detectors for sulphur. S_2-species are generated in the flame and the radiation emitted by them is measured in the UV range. A preliminary separation of sulphur, *e.g.* by chromatography, is required for analysis of samples in which sulphur is associated with hydrocarbons, as in gas, fuel and petroleum samples, since hydrocarbons cause the emission to be diminished in proportion to both the concentration and number of carbon atoms per molecule of hydrocarbon. The quenching effect on the emission by carbon present as dioxide is negligible when compared with its effect when present as hydrocarbon. This finding has led to the use of preliminary oxidation to avoid the need of prior separation. A complete apparatus, which includes a stacked burner system, is described. Continuous monitoring of sulphur in a stream of hydrocarbon gases is possible.

W. E. RUPPRECHT AND T. R. PHILLIPS,
Anal. Chim. Acta, 47 (1969) 439–449

INORGANIC ELECTRONIC SPECTROSCOPY

by A. B. P. LEVER, Associate Professor of Chemistry,
York University, Toronto, Canada

The first monograph in the series PHYSICAL INORGANIC CHEMISTRY, edited by M. F. LAPPERT

Electronic spectroscopy has become, in recent years, a commonplace tool in inorganic research and development although few books dealing with the topic have appeared. Those books dealing with spectroscopy in general devote but a few pages to a discussion of the electronic spectra of inorganic compounds.

The aim of this book is (a) to provide the reader with a basic understanding of the methods and procedures involved in a study of the electronic spectra of inorganic compounds, (b) to discuss the information which may be derived from such study, with particular emphasis on stereochemistry and chemical bonding, and (c) to provide a reference text.

A beginning is made at a level which can be understood by an average student with a first degree, the first third of the book dealing with atomic theory, symmetry and group theory. In progressing further with the material presented, the reader can proceed from the construction of qualitative energy level diagrams and the assignment of transitions observed in the spectra of cubic molecules, to quantitative diagrams and the spectra of non-cubic molecules.

Having mastered this material the reader is shown how to derive useful information concerning stereochemistry and chemical bonding and even, qualitatively, such properties as effective nuclear charge and mean *d*-orbital radii. The spectra of the more common transition metal ions in their many oxidation states and stereochemistries are discussed in Chapter 9, which is a mine of information for the practising inorganic spectroscopist.

The book is unique in being the only reference work available which will bring the new graduate up to the level where he can read and usefully digest the original research papers in inorganic spectroscopy. Much of the material has not appeared in book form before and some of it has not appeared in print at all.

Contents: Preface. 1. Atomic structure. 2. Molecular symmetry. 3. Group theory. 4. Crystal field diagrams. 5. Term diagrams. 6. Selection rules, band intensities and dichroism. 7. Some theoretical aspects of electronic spectra. 8. Charge transfer spectra. 9. Crystal field spectra. Appendices. Indexes.

xii + 420 pages, 78 tables, 130 illus., 465 lit. refs., 1968, Dfl. 90.00, £11.10.0.

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A SPECTROPHOTOMETRIC STUDY OF THE IRON(III)–PHENOL REACTION

Iron(III) reacts with phenol to form a weakly associated complex in the ratio of 1:1. The weak association of iron(III) with phenol necessitates a correction for significant interference by dimerization of iron(III) due to hydrolysis, particularly at pH 1.4 and 2.0. It seems probable that a slower secondary reaction between iron(III) and phenol proceeds with the formation of iron(II) and a phenolic oxidation.

G. Limb and R. J. Robinson,
Anal. Chim. Acta, 47 (1969) 451–460

THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN ILMENITE

A new procedure has been developed for eliminating interference from titanium in the N-benzoyl-N-phenylhydroxylamine procedure for determination of vanadium. After the oxidation of vanadium(IV) with potassium permanganate, vanadium(V)–BPHA complex is extracted into chloroform from sulphuric acid and converted to the chloride form before removal of the original aqueous phase. Co-extracted titanium is removed from the isolated organic phase by extracting with a solution of pentasodium tripolyphosphate in 2 *M* sulphuric acid. Appropriate arrangement of the order of reagent addition avoids reduction of vanadium(V) in the strongly acidic chloride systems.

E. S. Pilkington and W. Wilson,
Anal. Chim. Acta, 47 (1969) 461–468

SOME CONSIDERATIONS ON APPARENT DEVIATIONS FROM LAMBERT–BEER'S LAW

Apparent deviations from Lambert–Beer's law may be caused by chemical and/or physical effects, instrumental effects or both. A general procedure is described for distinguishing between these three types of effects. The validity of the procedure is verified by some measurements in the visible region of the spectrum, on cobalt(II) and plutonium(VI) solutions. The method is shown to be especially valuable for establishing the correlation between absorbance data, measured with different cell lengths.

K. Buijs and M. J. Maurice,
Anal. Chim. Acta, 47 (1969) 469–474

ION-SELECTIVE ELECTRODES IN CONTINUOUS-FLOW ANALYSIS

DETERMINATION OF CALCIUM IN SERUM

The use of a calcium-selective electrode as a sensor in procedures involving the AutoAnalyzer is described. The influence of various parameters such as temperature, pH, ionic strength, and carry-over, as well as interactions between the pump and electrodes, were studied. Quantities of calcium between $2 \cdot 10^{-6}$ and $1 \cdot 10^{-2}$ *M*/l were determined in synthetic aqueous samples, Merck standards for serum analysis, Seronorm standards of human serum, and non-standardized horse serum at a rate of 40 samples/h. The method was found to be simpler than colorimetry and also avoids dialysis, giving values of "free" calcium (calcium ion activity), which is clinically more important than total calcium content.

J. Růžička and J. C. Tjell,
Anal. Chim. Acta, 47 (1969) 475–482

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Comparison with the 6th edition reveals the following differences:

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Preliminary tests	32	45
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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.

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EFFECT OF ACETATE BUFFER ON THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANUM USING A LANTHANUM FLUORIDE MEMBRANE ELECTRODE

Precipitation titrations of fluoride with lanthanum nitrate using a lanthanum fluoride electrode have been carried out at constant ionic strength and different acetate concentrations. The titration curves have been analysed by rigorous equilibrium calculations with the computer program HALTAFALL. Acetate ions have been shown to enter the solid phase, forming precipitates with the formula $LaF_{3-x}Ac_x$ $(0<x<1)$. The presence of acetate causes the electrode to work sluggishly and to deviate from the Nernst law. These effects increase with increasing acetate concentrations and may possibly even occur at high nitrate concentrations.

T. Anfält and D. Jagner,
Anal. Chim. Acta, 47 (1969) 483–494

DETERMINATION OF VALENCE STATES OF IRON IN GLASS AND OF URANIUM IN CALCIUM FLUORIDE SINGLE CRYSTALS

The instantaneous oxidation of macro and semi-micro amounts of iron(II) in various types of glasses, of iron(II) in magnesium oxide, and of semi-micro quantities of uranium(III) or uranium(IV) in calcium fluoride single crystals by excess of cerium(IV) present in the solvent system, followed by back-titration with iron(II) ammonium sulfate, is the basis for a simple, accurate method which, furthermore, obviates the need for an inert atmosphere. Formal oxidation potentials of the Ce(IV)/Ce(III) couple and the Fe(III)/Fe(II) couple in the hydrofluoric–sulfuric acid glass-dissolving mixture were estimated.

U. Abed,
Anal. Chim. Acta, 47 (1969) 495–502

FLUORIMETRIC DETERMINATION OF OXIDATIVE ENZYMES

ANALYTICAL APPLICATIONS OF THE MONOAMINE AND DIAMINE OXIDASE SYSTEMS

Fluorescence methods are described for the assay of the oxidative enzymes, monoamine and diamine oxidase. The method is based on the conversion of the non-fluorescent *p*-hydroxyphenylacetic acid to a highly fluorescent fluorophore by hydrogen peroxide and peroxidase. The initial rate of formation of this fluorescent compound is measured and related to the activity of the enzymes. The substrates of these enzyme systems—benzylamine, tyramine, furfurylamine, cadaverine, histamine, and putrescine—can be determined in microgram concentrations with a precision and accuracy of better than 3%. The reagent *p*-hydroxyphenylacetic acid is stable and can be used for several months.

G. G. Guilbault, S. S. Kuan and P. J. Brignac, Jr.,
Anal. Chim. Acta, 47 (1969) 503–509

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THE DETERMINATION OF COPPER IN CADMIUM SULPHIDE

(in French)

Two methods are described for the determination of copper in cadmium sulphide. Copper concentrations of the order of 10^{-6} g per g of cadmium sulphide can be determined spectrophotometrically by means of the cuprizone complex, whereas 10^{-5} g/g can be determined by atomic absorption spectrophotometry, with a precision of about 5%. For smaller amounts, or when the sample size is limited ($<$ 40 mg), atomic absorption spectrophotometry must be used.

F. Cabane-Brouty,
Anal. Chim. Acta, 47 (1969) 511–516

DECOMPOSITION BY PRESSURE IN INORGANIC ANALYSIS

A suitable apparatus for pressure decomposition of refractory inorganic materials with acids is described. The materials are heated under pressure in a steel autoclave lined with a PTFE crucible in a thermostatted oven fitted so that the autoclaves can be rotated. The decomposition process is hastened not only by pressure but also by continuous agitation. The decomposition of corundum was studied in detail. The proposed decomposition method was sucessfully applied to the analysis of titanium and tin dioxides, ferrites, boron nitride and several resistant rocks and minerals. Different acid mixtures are recommended for different materials; a pure silicon dioxide solution was easily prepared by pressure dissolution with potassium hydroxide. The methods are very suitable for routine use.

J. Doležal, J. Lenc and Z. Šulcek,
Anal. Chim. Acta, 47 (1969) 517–527

CHEMICAL IMPRECISION IN THE SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH DITHIO-OXAMIDE

The precision of a single spectrophotometric determination of ruthenium as the dithio-oxamide complex is shown to be about 0.5% and to be limited by chemical rather than instrumental irreproducibility. The molar absorptivity of this complex is $(1.11 \pm 0.02) \cdot 10^4$ l/mole-cm at 654 nm, considerably smaller than reported previously. It is shown that solutions of ruthenium for use as spectrophotometric standards may be prepared with a precision of about 0.3% by dissolving weighed portions of the pure metal powder in alkaline sodium hypochlorite at pH *ca.* 10, taking precautions to avoid the loss of RuO_4 during the dissolution.

P. J. Lingane,
Anal. Chim. Acta, 47 (1969) 529–537

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THE PHOTOMETRIC DETERMINATION OF TRACES OF LEAD BY MEANS OF 7-[α-(*o*-CARBOMETHOXYANILINO)-BENZYL]-8-HYDROXYQUINOLINE

(in German)

Traces of lead can be extracted and determined spectrophotometrically by means of CMAB-oxine. The molar absorptivity is $4.5 \cdot 10^3$ at 410 nm. The determination is highly selective in the presence of suitable masking agents; the influence of Al, Bi, Ca, Cd, Co, Cu, Fe, In, Mg, Mn, Na, Ni, Tl, Zn was examined. Bismuth is co-extracted by the reagent, but lead can be determined by a modified, less sensitive procedure.

G. Röbisch,
Anal. Chim. Acta, 47 (1969) 539–546

SPECIFIC DETERMINATION OF AMERICIUM WITH A RECORDING SPECTROPHOTOMETER

(Short Communication)

K. Buijs, B. Chavane de Dalmassy and M. J. Maurice,
Anal. Chim. Acta, 47 (1969) 547–550

SUBSTITUTED MALONIC ACIDS AS SOLVENT EXTRACTION REAGENTS

(Short Communication)

J. Aggett and M. H. Timperley,

Anal. Chim. Acta, 47 (1969) 551–553

SPOT TESTS FOR MERCAPTO COMPOUNDS

(Short Communication)

F. Feigl, D. Goldstein and E. K. Libergott,
Anal. Chim. Acta, 47 (1969) 553–555

NOTE ON THE ELIMINATION OF ANIONS WHICH CONTAIN REACTIVE BIVALENT SULFUR

(Short Communication)

F. Feigl and A. Caldas,
Anal. Chim. Acta, 47 (1969) 555–557

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R. ZWEIDINGER, L. B. SANDERS AND J. D. WINEFORDNER,
Anal. Chim. Acta, 47 (1969) 558–559

DETERMINATION OF TRACE ELEMENTS IN SEAWATER BY NEUTRON ACTIVATION ANALYSIS

(Short Communication)

D. Z. PIPER AND G. G. GOLES,
Anal. Chim. Acta, 47 (1969) 560–563

THE DETERMINATION OF IRON BY ATOMIC FLUORESCENCE SPECTROSCOPY WITH A MODULATED MICROWAVE-EXCITED ELECTRODELESS DISCHARGE TUBE

(Short Communication)

L. EBDON, G. F. KIRKBRIGHT AND T. S. WEST,
Anal. Chim. Acta, 47 (1969) 563–568

SEPARATION OF RHENIUM FROM MOLYBDENUM, TUNGSTEN, VANADIUM AND SOME OTHER ELEMENTS BY EXTRACTION WITH ISOAMYL ALCOHOL FROM PHOSPHORIC ACID–HYDROGEN PEROXIDE

(Short Communication)

V. YATIRAJAM AND L. R. KAKKAR,
Anal. Chim. Acta 47 (1969) 568–570

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH 2-AMINOCYCLOPENTENE-1-DITHIOCARBOXYLIC ACID

(Short Communication)

N. K. DUTT AND T. SESHADRI,
Anal .Chim. Acta, 47 (1969) 571–572

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With Applications to Photochemistry and Analytical Chemistry

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Atomic-Absorption Spectroscopy

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NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART V. SIMULTANEOUS DETERMINATION OF METALLIC IMPURITIES

C. BALLAUX, R. DAMS AND J. HOSTE
Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

(Received June 23rd, 1969)

In previous papers the determinations of the principal nonmetallic impurities in selenium were reported, *i.e.* chlorine, bromine, iodine, tellurium, sulfur and phosphorus[1-4].

In the present work the determination of metallic impurities is described. The elements sodium, potassium, chromium, iron, cobalt, copper, zinc, gallium, silver, cadmium, tungsten, gold and thallium have already been determined in high-purity selenium[5-15]. In these procedures a separation of selenium is performed (except for the method of WILLIAMS[11]) by precipitation in the elementary state; afterwards each impurity is isolated from the other activities and counted.

In the present investigation, a faster procedure is applied. By (n,γ), (n,p), (n,α) and (n,γ,β^-) reactions on the matrix, important activities from selenium, arsenic, germanium, bromine and krypton, respectively, are produced. All are separated by volatilisation. The metallic impurities which form γ-emitting isotopes by neutron irradiation are determined simultaneously by high-resolution Ge-Li γ-spectrometry. The ^{204}Tl, a pure β-emitter is afterwards precipitated and counted with a G.M.-tube.

Nuclear data and interferences

The most pertinent nuclear data of the radionuclides produced by neutron irradiation of 15 elements, are shown in Table I. Only the data pertaining to the radioisotopes which are used in the present activation analysis are mentioned. Most of the possible nuclear interferences caused by threshold reactions can be neglected because the cross-sections are generally 1000 times smaller than those for (n,γ) reactions[17]. Only the interference of the threshold reaction ^{59}Co(n,p)^{59}Fe ($\sigma\cdot\theta = 1.7$ mb) on the reaction ^{58}Fe(n,γ)^{59}Fe ($\sigma\cdot\theta = 3.0$ mb) may be important. Fortunately, the iron content of selenium is higher than its cobalt content and the fast neutron flux is at least 10 times lower than the thermal neutron flux at the irradiation site.

EXPERIMENTAL

Preparation of samples and standards. Irradiation conditions

Samples (100 mg) were sealed in silica tubes and irradiated for 3 days at a neutron flux of 10^{13} n cm^{-2} sec^{-1} (BR-2 reactor). As standard, a mixture of the 14 elements which give rise to γ-emitting isotopes, was prepared in μg or ng amounts

TABLE I

NUCLEAR DATA OF THE ELEMENTS DETERMINED

Stable isotope	*Abundance (%)*	*Cross-section (b)*	*Produced isotope*	*Selected γ-transition(s) (keV)*	*Half-life*
^{23}Na	100	0.53	^{24}Na	1368.4	15.0 h
^{41}K	6.91	1.1	^{42}K	1524.7	12.52 h
^{45}Sc	100	22	^{46}Sc	889.4–1120.3	83.9 d
^{50}Cr	4.31	13.5	^{51}Cr	320.0	27.8 d
^{58}Fe	0.31	0.98	^{59}Fe	1098.6–1291.5	45.1 d
^{59}Co	100	31	^{60}Co	1173.1–1332.4	5.24 y
^{63}Cu	69.1	4.3	^{64}Cu	511.0 (β^+)	12.9 h
^{64}Zn	48.89	0.44	^{65}Zn	1115.4	245 d
^{71}Ga	39.8	4.0	^{72}Ga	630.1–834.1	14.3 h
^{109}Ag	48.65	3.2	^{110m}Ag	657.8–884.5	245 d
^{114}Cd	28.86	1.1	^{115}Cd		53.5 h
			^{115m}In daughter	336.6	
^{139}La	99.94	8.2	^{140}La	328.6–486.8	40.2 h
^{186}W	28.4	34	^{187}W	479.3–685.7	23.9 h
^{197}Au	100	96	^{198}Au	411.8	2.70 d
			^{199}Au	158.3	3.15 d
^{203}Tl	29.5	8	^{204}Tl		3.56 y

so as to induce about the same ratios of the activities in the mixture as in the selenium samples but with a 50 to 100 times higher intensity. Copper–gold and sodium–thallium standards were also irradiated simultaneously.

To correct for flux gradients in the capsule, a 1% cobalt–aluminium wire was stretched in the center of the capsule over the whole length and half its width. As appeared from the specific activities of the different pieces of the wire, no flux depression could be detected.

Chemical separation

The behaviour of 23 elements in sulfuric acid–hydrobromic acid medium at 200–220° was investigated by tracer experiments. Tracer solutions of high specific activity (μg amounts) were added to 1 g of selenium and 1 mg of arsenic. For the elements tin, antimony, mercury, tellurium, molybdenum, thallium and gold, however, mg amounts have to be added. From the results listed in Table II, it appears that good agreement was obtained with the experiments of Hoffman and Lundell[18]. Hoffman and Lundell[18] also reported that no distillation occurred for Al, Ba, Be, Ca, Cs, Hf, In, Ir, Li, Nb, Ni, Pb, Pd, Pt, Rb, Rh, Si, Ta, Th, Ti, U and Zr. It can be seen that the matrix activities from selenium, arsenic, germanium and bromine isotopes are almost quantitatively separated. Of the other elements investigated only tin, rhenium, antimony, mercury and the halogens are co-distilled. More than 99% of all the metals under investigation remain in the sulfuric acid solution, with the exception of gold, of which only a few percent is distilled. By the addition of carrier the volatilisation of gold can be decreased and the yield can be determined afterwards. Tracer experiments further proved that the pure β-emitter ^{204}Tl could be separated as tetrathioureum thallium(I) perchlorate and thallium(I) chromate.

TABLE II

BEHAVIOUR OF DIFFERENT ELEMENTS IN H_2SO_4–HBr AT 200–220°

Element	*% distilled*		*Element*	*% distilled*	
	Hoffman-Lundell gravimetry[18]	*Present work Tracer*		*Hoffman-Lundell gravimetry*[18]	*Present work Tracer*
As(III) or (V)	100	>99.999	Mn	0.02	
Re	100		Ag	0	0.5
Se(IV) or (VI)	100	>99.999	Cd	0	0.4
Sn(II) or (IV)	100	>99.98	Co	0	<0.1
Sb(III)	99.8	93.5	Cr(III)	0	0.2
(V)	98		Cu	0	0.8
Ge	95		Fe	0	<0.1
Hg(I) or (II)	90	97.2	Ga	0	<0.1
Te(IV) or (VI)	10	15.7	K	0	0.1
B	10		Na	0	<0.1
Mo	4	1.2	Sc	0	0.2
P	1	1.2	W	0	0.5
Tl	1	0.6	Zn	0	<0.1
Bi	1		R.E.	0	0.2 (La)
Au	0.5	34.6–8.3 226 μg 14.3 mg			

Counting

The residue of a distillation of 100 mg of irradiated selenium was measured during ±10 h with a 18-cm^3 Ge(Li) detector 2–4 days after the end of irradiation. After the decay of the relatively short-lived isotopes (at least 12 days after the end of irradiation) the sample was again measured for the determination of the long-lived species. This detector was used with a preamplifier–amplifier combination coupled to a 20 Mc analog-to-digital converter and a 4096-channel analyser. The integration and differentiation constants were 1.6 μsec. All the equipment was used in a temperature-controlled counting room (±0.5°). The gain stability was better than 1 keV/24 h. The FWHM was 3.2 keV for the 1332.4-keV peak of ^{60}Co.

The γ-spectra are shown in Figs. 1 and 2. At first a qualitative analysis was performed; therefore the energies of the photopeaks present in the γ-spectrum were determined.

The most intense lines of the isotopes ^{131}I, ^{177}Lu, ^{139}Ce, ^{203}Hg, ^{198}Au, ^{22}Na, ^{207}Bi, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{60}Co and ^{24}Na were used to calibrate the spectrometer. The energies found were compared with the values given in the literature[19]. In general, excellent agreement was obtained, *i.e.* a deviation of less than 0.5 keV. More certainty about the identity of certain isotopes was obtained from decay analyses. The following isotopes could be identified in the residue of the distillation: ^{24}Na, ^{42}K, ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn, ^{72}Ga, ^{110m}Ag, ^{115}Cd, ^{140}La, ^{187}W, ^{198}Au and ^{199}Au.

The photopeaks used for the quantitative determinations are indicated in Table I. The number of counts in 7 channels around the peak top were summed. This corresponds to 7 keV or twice the FWHM. Because the total count rate never exceeded 10^3 c sec^{-1}, no deterioration of the resolution occurred during the analyses.

Copper could only be determined from the annihilation radiation at 511 keV, after subtraction of the contribution in this energy region from ^{24}Na and from the background.

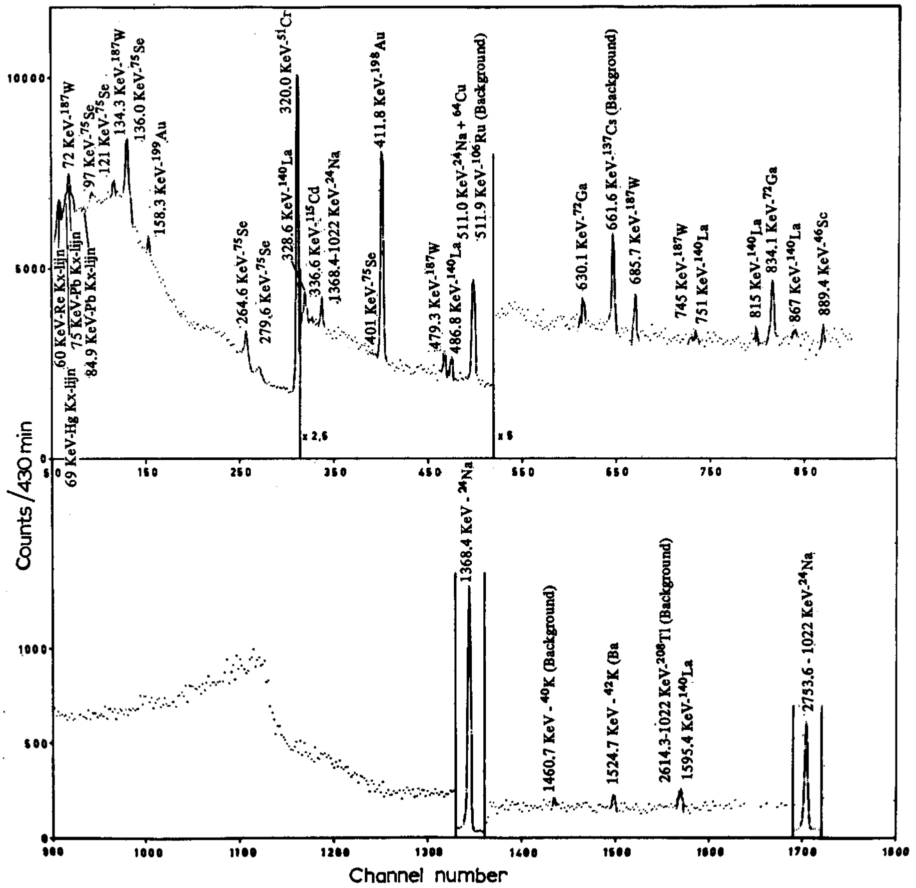

Fig. 1. γ-Spectrum of an unknown sample measured 3 days after the end of the irradiation.

As appeared from a simultaneously irradiated pure gold standard, the isotope ^{199}Au was formed exclusively from the second-order interference ^{197}Au(n,γ)^{198}Au(n,γ)-^{199}Au. A possible contribution from ^{198}Pt(n,γ)^{199}Pt(β^-)^{199}Au could not be detected.

After the γ-spectrometric measurements, ^{204}Tl was precipitated and counted with a G.M.-tube. Owing to the low counting rates, the radiochemical purity of the thallium chromate precipitates could not be controlled by absorption or decay curve analysis (E_{β^-}(max) = 766 keV). When the precipitates were measured over a period of 160 days, no marked decrease of the counting rates could be observed. This is in agreement with the literature ($T_{\frac{1}{2}}$ = 3.56 y). Furthermore, no γ-emission could be detected by γ-spectrometry. The precipitates thus do not contain β-emitters with a half-life shorter than that of ^{204}Tl, or any γ-emitters.

Procedure

Cool the samples for one day. Etch with 4 *N* nitric acid, wash with water, dry and weigh. Dissolve in 10 ml of 14 *N* nitric acid. Add 1 mg of arsenic, 10 mg of gold and 10 mg of thallium and distill from sulfuric acid–hydrobromic acid medium at

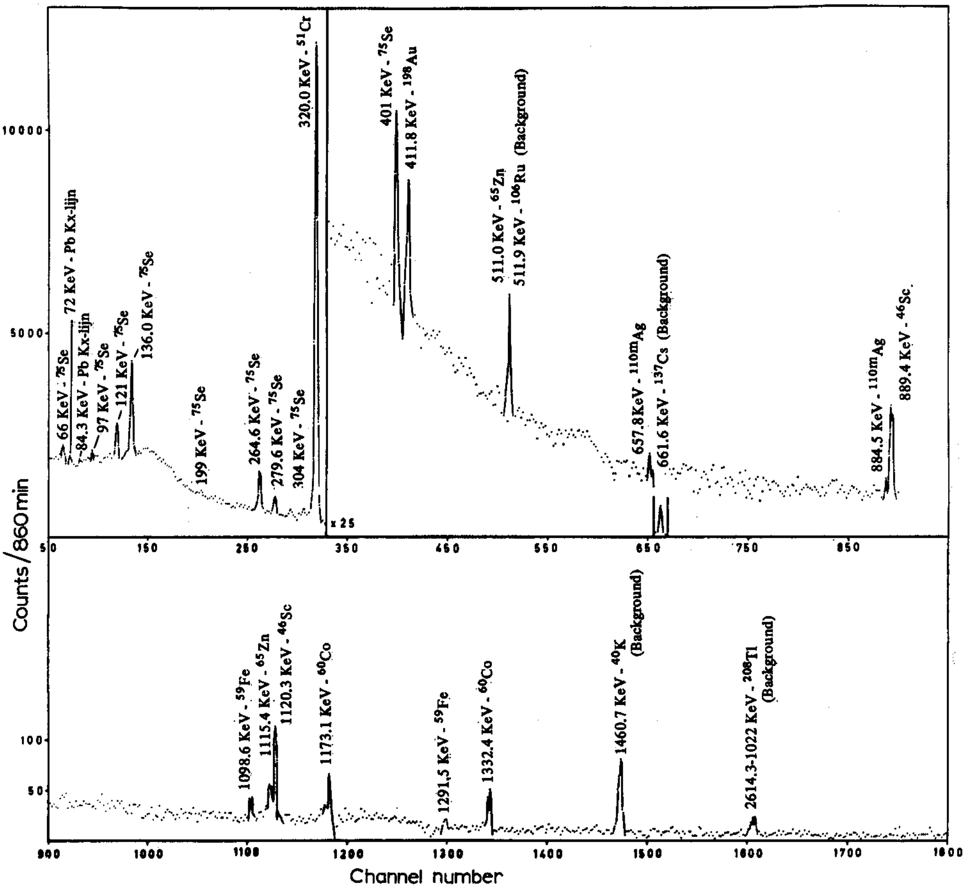

Fig. 2. γ-Spectrum of an unknown sample measured 15 days after the end of the irradiation.

200–220° as described previously[3]. Dissolve the gold precipitate, formed in the distillation flask by reduction with hydrobromic acid, by addition of a few ml of 14 N nitric acid.

Make the residue of the distillation up to 50 ml in a calibrated flask and measure with the Ge(Li) detector. Dissolve the mixture of the standards in *aqua regia* and 15 ml of 35 N sulphuric acid. Make the solution up to 50 ml and count during 45 min just before the measurement of each sample. Use the sodium and the copper standards to determine the contribution of both isotopes to the count rate at 511 keV. Measure the gold standard to calculate the contribution of gold to the count rate of the photopeak at 158 keV, due to ^{199}Au. Measure the sample and the standards again, at least 12 days after the irradiation.

After the measurement of the γ-emitting isotopes, evaporate the solution on a boiling water bath. Precipitate gold with sulfurous acid. Dissolve the gold precipitate in a minimum amount of *aqua regia* and evaporate to dryness. Add 15 ml of 3 N hydrochloric acid and extract gold with 30 and 10 ml of ethyl acetate. Evaporate the collected organic phase to dryness, dissolve the residue in 10 ml of 6 N hydrochloric acid, reprecipitate gold and weigh to determine the yield.

For the determination of thallium, evaporate the filtrate of the first precipitation to *ca.* 3 ml and add 50 ml of water, 10 ml of 70% perchloric acid and 50 ml of 10% thioureum solution. After cooling for 1 h in ice water, the $TlClO_4 \cdot 4(NH_2)_2CS$ precipitate is formed. Filter, dissolve the precipitate in 15 ml of hot water, and add 2 ml of 6 *N* ammonium hydroxide and 4 ml of 10% potassium chromate solution. Digest overnight, filter and wash the precipitate three times with 1% potassium chromate solution and four times with 50% ethanol. Dry for 1 h at 110°, weigh as thallium(I) chromate and count with a G.M.-tube. Dissolve the thallium standard, add 10 mg of carrier, precipitate, weigh and count.

RESULTS AND DISCUSSION

In three different selenium samples the amounts of sodium, potassium, scandium, chromium, iron, cobalt, copper, zinc, gallium, silver, cadmium, lanthanum, tungsten, gold and thallium were determined. The results and the standard deviations on the counting are given in Table III. The most important impurities present in the selenium are sodium, potassium, copper and chromium. The presence of chromium is probably due to the preparation of the selenium in stainless steel crucibles. For iron, zinc, silver, cadmium, and thallium the amounts present are below the detection

TABLE III

RESULTS OF DETERMINATIONS IN SELENIUM

Element determined	*Sample concentration found*		
	1	*2*	*3*
Na (p.p.m.)	2.61 ± 0.08 (3.1%) 2.06 ± 0.03 (1.5%)	2.51 ± 0.03 (2.0%) 2.40 ± 0.05 (2.1%)	1.66 ± 0.02 (1.2%) 1.48 ± 0.03 (2.0%)
	2.34	2.46	1.58
K (p.p.m.)	2.1 ± 0.5 (24%) 1.9 ± 0.6 (32%)	≦ 1.6 ≦ 1.5	≦ 1.3 ≦ 1.2
	2.0	≦ 1.6	≦ 1.3
Cr (p.p.m.)	3.01 ± 0.03 (1.0%) 3.15 ± 0.05 (1.6%)	2.56 ± 0.05 (2.0%) 2.25 ± 0.04 (1.8%) 3.30 ± 0.03 (0.9%)	3.08 ± 0.07 (2.3%) 3.36 ± 0.05 (1.5%) 2.43 ± 0.03 (1.2%) 2.09 ± 0.05 (2.4%)
	3.07	2.67	2.73
Fe (p.p.m.)	≦ 0.7 ≦ 0.9	≦ 1.4 ≦ 0.9 ≦ 0.6	≦ 0.9 ≦ 0.5 ≦ 1.3 ≦ 0.3
	≦ 0.8	≦ 0.8	≦ 0.8
Co (p.p.b.)	6.0 ± 0.6 (10%) 4.3 ± 0.9 (21%)	≦ 3.2 ≦ 1.5 ≦ 1.4	≦ 1.6 ≦ 1.3 ≦ 2.4 ≦ 2.7
	5.1	≦ 2.0	≦ 2.0

TABLE III *(continued)*

Element determined	*Sample concentration found*		
	1	*2*	*3*
Cu (p.p.b.)	150 ± 12 (8.0%) 130 ± 20 (15%)		134 ± 6 (4.5%) 217 ± 9 (4.1%)
	140		176
Zn (p.p.b.)	82 ± 24 (29%) ≦ 87	≦ 108 ≦ 52 ≦ 71	≦ 58 ≦ 43 ≦ 50 ≦ 46
	≦ 85	≦ 77	≦ 49
Ga (p.p.b.)	53 ± 5 (9.4%) 50 ± 6 (12%)	56 ± 9 (16%) 102 ± 24 (23%)	35 ± 8 (23%) ≦ 20
	51.^{5}	79	≦ 28
Sc (p.p.b.)	0.83 ± 0.05 (6%) 0.70 ± 0.05 (7%)	0.63 ± 0.06 (9.5%) 0.52 ± 0.04 (7.7%) 0.70 ± 0.11 (16%)	0.58 ± 0.05 (8.8%) 1.08 ± 0.05 (4.9%) 0.20 ± 0.05 (26%) 0.65 ± 0.10 (15%)
	0.77	0.63	0.63
Ag (p.p.b.)	— ≦ 3	≦ 7 ≦ 13 ≦ 7	≦ 7 ≦ 6 ≦ 5 ≦ 2
	≦ 3	≦ 9	≦ 5
Cd (p.p.m.)	≦ 7	≦ 2 ≦ 7	≦ 39 ≦ 25 ≦ 4
	≦ 7	≦ 3	≦ 15
La (p.p.b.)	4.7 ± 1.1 (25%) 2.7 ± 0.7 (25%)	5.1 ± 0.5 (9.8%) 4.4 ± 1.1 (25%) 12 ± 1 (8.3%)	3.2 ± 0.9 (28%) 7.0 ± 1.8 (26%) ≦ 3.0 2.7 ± 0.7 (26%)
	3.7	7.2	4.0
W (p.p.b.)	21 ± 4 (19%) 8.9 ± 1.4 (16%)	27 ± 3 (11%) ≦ 3 ≦ 15	
	15	≦ 15	
Au (p.p.b.)	0.83 ± 0.05 (6.0%) 1.2 ± 0.1 (8.3%)	2.7 ± 0.2 (2.3%) 3.6 ± 0.15 (4.2%) 0.59 ± 0.02 (3.6%)	0.86 ± 0.06 (7.0%) 0.37 ± 0.04 (11%) 0.48 ± 0.03 (6.3%) 1.31 ± 0.03 (2.3)
	1.0	2.3	0.76
Tl (p.p.m.)	≦ 0.08 ≦ 0.13	≦ 0.03 ≦ 0.14 ≦ 0.09	≦ 0.13 ≦ 0.04 ≦ 0.12 ≦ 0.14
	≦ 0.11	≦ 0.09	≦ 0.11

limit. The activities deriving from gallium, lanthanum and tungsten are below the determination limit. The low reproducibility of the determination for several trace elements is probably due to inhomogeneous distribution of the impurities in the highly pure selenium.

The authors are grateful to Mr. Tombu, Metallurgie Hoboken, for providing the selenium samples, and Mr. E. Everaert for technical assistance.

SUMMARY

Neutron activation analyses for Na, K, Cr, Fe, Co, Cu, Zn, Ga, Ag, Cd, La, W, Au and Tl in high-purity selenium in the p.p.m. and p.p.b. ranges were performed by irradiating 100-mg samples together with standards at a flux of 10^{13} n cm^{-2} sec^{-1}. The matrix activities from selenium, arsenic, germanium and bromine isotopes were separated by distillation in sulphuric acid–hydrobromic acid at 200–220°. The γ-emitting isotopes were measured simultaneously by γ-spectrometry with a Ge(Li) detector. The pure β-emitter ^{204}Tl was precipitated as tetrathiourea thallium(I) perchlorate and thallium(I) chromate and counted with a G.M.-tube.

RÉSUMÉ

On a effectué des analyses par activation neutronique de Na, K, Cr, Fe, Co, Cu, Zn, Ga, Ag, Cd, La, W, Au et Tl dans un sélénium très pur, à des concentrations de l'ordre du p.p.m. ou du p.p.b. Ce procédé consiste à irradier des échantillons de 100 mg, avec étalons, à un flux de 10^{13} n cm^{-2} sec^{-1}. Les activités de la matrice dues aux isotopes de sélénium, d'arsenic, de germanium et de brome sont séparées par distillation dans le mélange acide sulfurique–acide bromhydrique à 200–220°. Les isotopes émis γ sont mesurés simultanément par spectrométrie γ avec détecteur Ge(Li). Le ^{204}Tl émetteur β est précipité comme perchlorate de tétrathiourée thallium(I) et chromate de thallium(I), et compté avec un tube G.M.

ZUSAMMENFASSUNG

In hochreinem Selen wurden durch Bestrahlen von 100 mg-Proben mit einem Neutronenfluss von 10^{13} n cm^{-2} sec^{-1} folgende Elemente im p.p.m.- und p.p.b.-Bereich aktivierungsanalytisch bestimmt:
Na, K, Cr, Fe, Co, Zn, Ga, Ag, Cd, La, W, Au und Tl. Die Matrixaktivitäten der Selen-, Arsen-, Germanium- und Brom-Isotope wurden durch Destillation aus Schwefelsäure–Bromwasserstoffsäure bei 200–220° abgetrennt. Die Isotope wurden gleichzeitig γ-spektrometrisch mit einem Ge(Li)-Detektor gemessen. ^{204}Tl als reiner β-Strahler wurde als Tetrathioharnstoffthallium(I)-Perchlorat und als Thallium(I)-Chromat gefällt und mit einem Geiger-Müller-Zählrohr registriert.

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THE DETERMINATION OF SILICON BY FLAME PHOTOMETRY AND ATOMIC FLUORESCENCE SPECTROSCOPY WITH A SEPARATED NITROUS OXIDE–ACETYLENE FLAME

R. M. DAGNALL, G. F. KIRKBRIGHT, T. S. WEST AND R. WOOD
Chemistry Department, Imperial College, London, S.W.7 (England)

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The determination of silicon by atomic absorption spectroscopy in the nitrous oxide–acetylene flame has been reported by a number of workers[1-4]. The application of a nitrogen- or argon-separated nitrous oxide–acetylene flame to improve the detection limit for the determination of silicon by flame photometry and atomic absorption has recently been reported[5,6]. Atomic fluorescence spectroscopy, with a commercially available flame spectrophotometer in conjunction with an electronically modulated silicon electrodeless discharge tube source[7], has been shown to produce good sensitivity for the determination of silicon. The optimal conditions for the determination of silicon by atomic fluorescence at 251.6 nm have been established. In the fuel-rich argon-separated flame, the determination is virtually specific, and a detection limit of 0.55 p.p.m. has been obtained under optimal conditions. The attainable detection limits for silicon by flame photometry and atomic fluorescence in the separated flame are compared with each other and with the detection limit obtained for atomic absorption at a conventional 50-mm slot burner with a high-intensity hollow-cathode lamp or an electrodeless discharge tube.

EXPERIMENTAL

Apparatus

The apparatus used was a Techtron AA4 atomic absorption spectrophotometer and Servoscribe recorder (0–10 mV), modified for atomic fluorescence measurements as described elsewhere[8,9]. Spectra were scanned with a 15-r.p.m. motor geared to the diffraction grating driveshaft. Silicon electrodeless discharge tubes (EDT) were employed for excitation of silicon atomic fluorescence. The discharge was maintained using a Microtron 200 microwave generator (2450 ± 25 MHz) (Electro-medical Supplies Ltd, London) electronically modulated at 285 Hz in phase with the Techtron AA4 amplification. The synchronous demodulator of the Techtron amplifier was phased to the modulated signal from the EDT by means of the synchronisation pulse provided by the Microtron modulator unit (variable 0 to 5 V p. to p. square wave). This signal was fed to the Techtron AA4 amplifier *via* the 5 pin DIN input socket provided on the AA4 to permit the use of a mechanical chopper. A quarter wave or three-quarter wave resonant cavity (Electro-medical Supplies Ltd, London Model 214L or 210L) was employed, and the discharge was initiated with a high-frequency "Tesla" vacuum-tester.

Burners

A Techtron AA4 50-mm path high-temperature burner (AB 40) was employed with the nitrous oxide–acetylene flame for atomic absorption measurements. Atomic emission and fluorescence studies were made with a circular burner with the nitrogen- or argon-separated and unseparated nitrous oxide–acetylene flame. This burner is identical to that described elsewhere[10] with the exception that in this study the flame was supported at a circular slot 0.75-mm wide and 11-mm internal diameter. Acetylene and nitrous oxide supplies to both burners were regulated by the gas control unit on the AA4 flame spectrophotometer. The indirect nebuliser of the Techtron was modified by the insertion of a 200-mm length of 10-mm diameter plastic tubing between it and the burner. This was found to provide greater flame stability.

Preparation of silicon electrodeless discharge tubes

Silicon discharge tubes were produced from elemental silicon and iodine by the same general procedure as previously described for other elements[11]. Some initial difficulty was experienced in the production of a silicon tube which produced an intense, stable discharge. A systematic study of the effect of varying the ratio of silicon to iodine on the intensity and stability of the output at 251.6 nm was, therefore, undertaken. The most satisfactory tubes were prepared containing silicon and iodine in the proportions of 7:1. These tubes, which were *ca.* 80-mm long, contained 5 mg of this mixture and were sealed at an argon filler-gas pressure of *ca.* 1 torr. The tubes produced greatest intensity and stability in the ¼-wave cavity when operated at 100 W (5 W reflected power). However, greater stability but less intense emission at the same power input may be obtained by use of the ¾-wave cavity. It was necessary to air-cool the tubes strongly to obtain stable output. Under these conditions the tubes showed a bright blue emission and the output was stable within a ±1% noise level. The warm-up period was about 5 min, and the long period fluctuation over a period of 1 h was less than ±3%, a value similar to that found for a silicon hollow-cathode lamp.

Spectral characteristics of discharge tube

The emission spectrum from the silicon discharge tube was obtained between

TABLE I

PRINCIPAL SOURCE EMISSION CHARACTERISTICS

Line (nm)	*Transition*	*Relative emission intensity*[a]	
		Hollow cathode lamp	*Electrodeless discharge tube*
250.69	$^3P_2{}^0 \rightarrow {}^3P_1$	2.1	89
251.43	$^3P_1{}^0 \rightarrow {}^3P_0$	2.1	69
251.61[b]	$^3P_2{}^0 \rightarrow {}^3P_2$	6.4	100
251.92	$^3P_1{}^0 \rightarrow {}^3P_1$	1.5	64
252.41	$^3P_0{}^0 \rightarrow {}^3P_1$	2.0	70
252.85	$^3P_1{}^0 \rightarrow {}^3P_2$	2.5	73

[a] Emission intensities expressed relative to intensity of 251.6 nm line from EDT.
[b] Most sensitive for atomic absorption.

200 and 260 nm. The only atomic silicon lines obtained were those between 250 and 253 nm shown in Table I. The intensities obtained under the same instrumental conditions from a Techtron high-intensity hollow-cathode lamp are also shown. The line-to-background ratio obtained at 251.61 nm for the electrodeless discharge tube was 130:1, while for the hollow-cathode lamp it was 44:1.

Optical arrangement

In the atomic fluorescence studies the flame was irradiated with an electrodeless discharge tube placed at an angle of 90° to the line from the flame to the monochromator entrance slit. The centre of the burner head was 100 mm from the entrance slit of the monochromator. In an alternative arrangement the centre of the burner head was set 245 mm from the monochromator entrance slit, and the convex lens (63 mm focal length) supplied for use in atomic absorption with the flame spectrophotometer was placed between the flame and the slit 116 mm from the slit. Very little difference in emission intensity was observed for these two arrangements but the latter was more convenient. The silicon discharge tube was placed in the resonant cavity as close to the flame as possible with a 50-mm transparent silica disc placed between the cavity and the flame to prevent draughts from the air-cooling of the tube within the cavity. No focussing was used.

Reagents

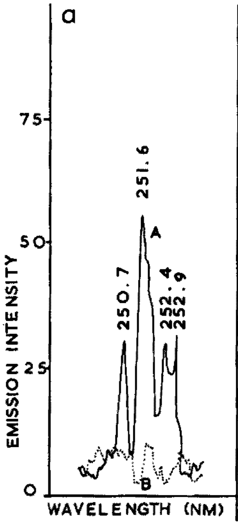
Stock silicon solution, 1,000 p.p.m. Dissolve 1 g of pure silicon powder (Hopkin and Williams Ltd) in sufficient cold concentrated hydrofluoric acid (AR grade, 40%) in a polythene bottle so that on dilution to 1 l with distilled water, the solution is 1% with respect to hydrofluoric acid.

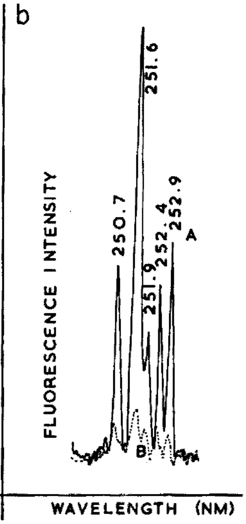
Diverse ions. Stock 10% solutions were prepared from analytical-reagent-grade salts of the elements.

RESULTS

The flame background and flame emission spectra for silicon between 249 and 254 nm are shown in Fig. 1a for the nitrogen-separated nitrous oxide–acetylene flame. The flame background is not intense in this region, but significant atomic emission is observed when silicon is introduced into the flame. Flame photometry thus provides good detection limits for silicon at 251.6 nm in the unseparated and separated flames. Lower detection limits are observed in the separated flame as a direct result of the lower background and noise levels in the interconal zone and because of the increased volume of the zone[5]. It has also been shown that the atomic population of silicon increases upon separation of a nitrous oxide–acetylene flame[6].

The flame background and atomic emission from silicon constitute a d.c. signal at 251.6 nm received by the photomultiplier. In the presence of this emission in the hot flame, therefore, it is necessary to employ a modulated source and detector if appreciable sensitivity and good selectivity are to be obtained in the detection of silicon by atomic fluorescence spectroscopy. When atomic fluorescence measurements were made with the electronically modulated electrodeless discharge tube arrangement described above, the relative fluorescence intensities at various wavelengths shown in Fig. 1b were obtained when optimal acetylene flow-rate and height of observation were used. No appreciable fluorescence radiation was detected when a silicon high-intensity hollow-cathode lamp was employed as source. Negligible interference from the source was received at the monochromator slit by reflection from the burner assembly. The signal obtained at 251.6 nm when silicon solutions were introduced into the flame was assigned as silicon fluorescence rather than scatter from particulate material in the flame. The experimental evidence for this is: (*a*) that appreciable absorption by silicon atoms was observed in a.a.s. with the same flame, source and samples; (*b*) that the introduction of a 20,000 p.p.m. solution of sodium tungstate into the flame caused no scatter of incident radiation from the silicon source; and (*c*) that no scattered Hg 253.6-nm radiation was observed when the silicon EDT was replaced by an intense mercury EDT and a 1,000 p.p.m. silicon solution was aspirated into the flame. The absence of interference from other elements in the determination of silicon under the conditions described here also supports the assignment.





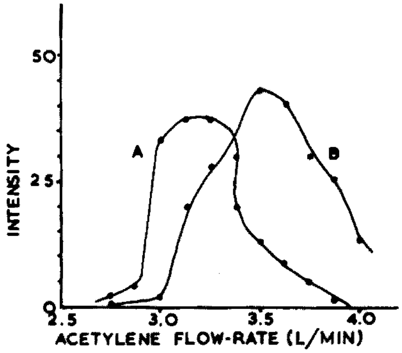


Fig. 1a. Flame spectrum for 100 p.p.m. silicon solution (A) and water blank (B) between 249 and 254 nm. Spectral slit-width 0.33 nm.

Fig. 1b. Atomic fluorescence spectrum for 6,000 p.p.m. silicon solution (A) and water blank (B) between 249 and 254 nm. Spectral slit-width 0.16 nm.

Fig. 2. Effect of acetylene flow-rate on emission intensity at 251.6 nm for 100-p.p.m. silicon solution (A), and on atomic fluorescence intensity at 251.6 nm for 50-p.p.m. silicon solution (B).

As shown in Fig. 1b, resonance fluorescence is observed at the principal silicon lines emitted from the source. The fluorescence at 251.4 nm ($^3P_1{}^0 \rightarrow {}^3P_0$) is difficult to resolve from the more intense emission at 251.6 nm and appears as a small shoulder on the 251.6-nm emission. Figure 1b also shows that at the spectral slit-width employed for greatest sensitivity, the monochromator transmits the fluorescence emission from all six lines, so that it is the integrated fluorescence intensity that is recorded as the analytical signal.

Optimum flame operating conditions

The flame operating conditions were chosen to produce the most intense atomic fluorescence signal with the minimum background and noise. A spectral slit-width of 0.99 nm was employed. The nitrous oxide flow-rate was maintained constant (5.8 l/min) and the nitrogen separating gas flow-rate was initially set at *ca.* 12 l/min. Under these conditions the effect of variation of the acetylene flow-rate on the fluorescence intensity and the atomic emission from silicon was investigated. Figure 2 shows that maximum fluorescence intensity is observed with *ca.* 3.5 l/min of acetylene, and this flow-rate was used in all further work. A minimum nitrogen flow-rate of 12 l/min was required to separate the flame zones effectively, but further increase in the flow-rate did not substantially affect the fluorescence signal intensity. With these optimum gas flow-rates established, the most intense fluorescence was observed in the red interconal zone of the flame immediately above the primary reaction zone. The slit viewed the interconal zone between 3 and 13 mm above the primary reaction zone.

Detection limits for silicon by flame photometry and atomic fluorescence

The limits of detection for silicon at 251.6 nm by atomic fluorescence and flame photometry were established for both separated and conventional flames. The detection limit for atomic absorption was determined at the conventional 50-mm slot burner. The detection limit was defined as the concentration of silicon in aqueous solution required to produce a signal: noise ratio of unity.

Under the appropriate optimum conditions of fuel flow-rate, height of observation and spectral slit-width (0.33 nm), the limits of detection obtained for silicon at 251.6 nm were 20 p.p.m. by flame photometry in the conventional flame, 6 p.p.m. in the nitrogen-separated flame and 5 p.p.m. in the argon-separated flame. For atomic fluorescence, the detection limit was 2 p.p.m. in the conventional flame and 0.7 and 0.55 p.p.m. in the nitrogen- and argon-separated flames, respectively. With the same apparatus and a silicon high-intensity hollow-cathode lamp with a 50-mm nitrous oxide–acetylene slot burner, the detection limit obtained by atomic absorption spectroscopy under optimum conditions was 4 p.p.m. A similar detection limit was obtained with the silicon electrodeless discharge tube as source.

Linear calibration graphs were obtained for silicon flame photometry in the nitrogen- or argon-separated flames at 251.6 nm over the range 25–500 p.p.m. For silicon atomic fluorescence in the nitrogen- or argon-separated flame, linear calibration graphs were obtained over the range 2–100 p.p.m. Over the range 50–1,000 p.p.m., slight curvature of the calibration graphs towards the concentration axis was observed.

Repetitive introduction (10 times) of a 200 p.p.m. silicon solution into the separated flames under the optimal conditions used to obtain the above calibration graphs indicated a relative standard deviation in the silicon flame emission intensity at 251.6 nm of 2.02%. Similar experiments with a 50-p.p.m. silicon solution resulted in a relative standard deviation of 1.8% for fluorescence measurements.

Interference studies

The effects of 100-fold amounts by weight of a range of cations and anions on the intensity of the atomic emission and atomic fluorescence produced by 100 p.p.m.

and 50 p.p.m. of silicon at 251.6 nm, respectively, were investigated. Foreign ions were considered not to interfere when they produced a variation in signal intensity of not greater than twice the standard deviation. The following did not affect either the atomic emission or atomic fluorescence intensities: Al, Be, Cd, Cu, Hg(II), K, Mg, Mn(II), Mo(VI), Na, Ni, Pb. Te(IV), Zn, Cl^-, NO_3^-, F^-, and PO_4^{3-}. The presence of a 100-fold weight of the following ions caused the error in silicon atomic emission at 251.6 nm given in parentheses: W(VI) (+300%), Fe(II) (+900%), V(V) (+1,000%), Cr(III) (+550%) and Co(II) (+700%). No interference, however, was observed from these ions on the atomic fluorescence intensity produced by 50 p.p.m. of silicon.

Conclusion

The hot, nitrogen- or argon-separated fuel-rich nitrous oxide–acetylene flame exhibits reducing properties which result in the maintenance of a substantially greater population of free ground state atoms of silicon than is obtained in a conventional nitrous oxide–acetylene flame supported at the same burner[5]. The high temperature permits effective excitation of the principal silicon resonance lines, so that good sensitivity is available in flame photometry. The determination of silicon by flame photometry in this way is also relatively free from physical and chemical interference effects. The selectivity of the determination of silicon by atomic fluorescence spectroscopy is higher, and with the modulated source and detection system employed, no spectral or physical interference from other species introduced into the flame is registered. The sensitivity of the atomic fluorescence determination, which was observed to be *ca.* one order of magnitude greater than for the determination by flame photometry, is dependent upon the line intensity and noise from the source, but is high even with the simple tubes whose preparation is described here.

We are grateful to Varian Techtron Pty. Ltd., Victoria, Australia for the provision of equipment and for the research studentship awarded to one of us (R.W.).

SUMMARY

The flame photometry and atomic fluorescence spectroscopy of silicon in nitrogen and argon separated nitrous oxide–acetylene flames have been investigated. The high-temperature, reducing, fuel-rich, argon-separated flame permits the detection of down to 5 and 0.55 p.p.m. of silicon in aqueous solution by flame photometry and atomic fluorescence, respectively. A silicon microwave-excited electrodeless discharge tube was prepared and used for excitation of the atomic fluorescence. The optimum conditions for the determination of silicon by both techniques have been investigated. The fluorescence technique showed no interference from hundredfold amounts (relative to silicon) of 23 ions, but 5 ions interfered in the determination by flame photometry. The fluorescence technique was also largely free from quenching and scatter effects in the presence of these extraneous ions.

RÉSUMÉ

Les auteurs ont effectué une étude sur la photométrie de flamme et la spectroscopie par fluorescence atomique du silicum en flamme oxyde nitreux (séparé de l'argon et de l'azote)–actétylène. Cette flamme, réductrice, à température élevée permet de déceler jusqu'à 5 et 0.55 p.p.m. de silicium dans une solution aqueuse, respectivement par photométrie de flamme et fluorescence atomique. On a préparé un tube à décharge spécial pour l'excitation de la fluorescence atomique. Les conditions optima sont données pour le dosage du silicium par ces deux techniques. La technique par fluorescence ne présente pas d'interférence pour 23 ions, en concentration 100 fois supérieure à celle du silicium, par contre cinq ions gènent le dosage par photométrie de flamme.

ZUSAMMENFASSUNG

Es wurde die flammenphotometrische und die atomfluoreszenzspektroskopische Bestimmung von Silizium mit stickstoff- und argon-getrennten Stickstoffoxid–Acetylen-Flammen untersucht. Die sehr heisse, reduzierende, brennstoffreiche argon-getrennte Flamme erlaubt den Nachweis von 5 bzw. 0.55 p.p.m. Silizium in wässriger Lösung mit der Flammenphotometrie bzw. Atomfluoreszenz. Es wurde eine durch Mikrowellen angeregte elektrodenlose Silizium-Entladungsröhre hergestellt und für die Anregung der Atomfluoreszenz verwendet. Die optimalen Bedingungen für die Bestimmung von Silizium mit beiden Techniken wurden bestimmt. Die Fluoreszenztechnik zeigt bei 23 Ionen im 100fachen Überschuss keine Störung; 5 Ionen störten die Bestimmung mit der Flammenphotometrie. Bei Gegenwart dieser Ionen war die Fluoreszenztechnik weitgehend frei von Quench und Streueffekten.

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USE OF INTEGRATION READOUT TECHNIQUES FOR LOW ABSORBANCE SAMPLES IN ATOMIC ABSORPTION SPECTROSCOPY

W. W. HARRISON AND F. E. BERRY
Department of Chemistry, University of Virginia, Charlottesville, Va 22901 (U.S.A.)

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The lower concentration limits of effective working solutions for atomic absorption spectroscopy are often set by the obtainable signal-to-noise ratio, a factor which involves the signal produced by the sample absorbance compared to the noise level or intrinsic instrumental uncertainty in the readout as determined by many factors, such as source intensity and amplifier stability. Lower concentration working limits naturally differ from one element to another but, in general, measurements which must be made at less than a 5% sample absorption may be subject to an increasingly unsatisfactory precision and accuracy unless stable scale expansion methods can be employed. A 1% uncertainty in setting the 0% absorption can create serious relative fluctuations in readout concentration at a particular instant in time. However, the factors contributing to signal fluctuation produce an uncertainty which is usually random as indicated by the rapid positive and negative excursions of the readout meter, recorder, or display. Addition of damping can often improve the situation at the expense of pen response. If the noise is truly random and the information signal unidirectional, it should be possible to recover a weak signal buried in noise by repetitively sampling the readout and allowing the information signal to accumulate, while the noise, at least to some extent, cancels itself out. Time averaging computers perform these functions very efficiently, but cost consideration precludes their widespread use at present.

A simpler approach to improvement of a poor signal-to-noise ratio lies in the use of integration techniques. By integrating a signal for a set period of time, it is possible to accumulate a charge which represents the net result of signal and noise. Again assuming that the noise is random, a readout signal is obtained which in the ideal case has a greatly enhanced information component and a noise component reduced to zero. In the more practical case, the information component is enhanced by charge accumulation while the noise component is moderated or, at least, builds at a less rapid relative rate. Both analog and digital integration techniques are available. The latter is a more elegant and accurate method and although presently more expensive and complex, both of these disadvantages are being reduced, and, as integrated circuit modules become more available, this technique should become more appealing and available to the budget-limited experimentalist. Analog integration techniques can also be quite accurate and are exceedingly simple and inexpensive with any of a great variety of solid-state operational amplifiers available today. For these reasons, analog integration techniques were used in this study. RODGERSON AND HELFER[1] used a ball and disc integration of recorder curves to correct for variations in flow rate while measuring iron in serum by atomic absorption spectrometry. Haagen-Smit and Ramirez-Muñoz[2] reported a multichannel integrating flame emission unit, while Öberg *et al.*[3] constructed a specialized flame photometer which utilized a micro-sample deposited onto a thin platinum wire and an operational amplifier integrator readout.

The ability to make effective use of very low absorbing samples can extend atomic absorption measurements into the p.p.b. working ranges normally ascribed to techniques such as spark source mass spectroscopy and neutron activation analysis. In this study, the determinations of magnesium and lead are used to illustrate the advantages of analog integration.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used to produce an absorption signal for integration. Figure 1 shows the scheme of the integration readout unit. An Amphenol two-conductor shielded cable feeds the off-balance signal voltage from the null meter to the input amplifier. This amplifier, while providing excellent isolation of the integrator from the spectrometer circuitry, is not absolutely necessary. Quite acceptable results can be obtained by feeding the signal directly to the 100 K resistor. Feedback current to the selected integration capacitor on the second amplifier produces an output voltage which is displayed across a voltage divider, the variable portion of which is a 10-turn miniature potentiometer. The 50K resistor may be shorted, depending upon signal magnitude. The signal is then recorded on a Sargent Model SRG potentiometric recorder. Switch S1

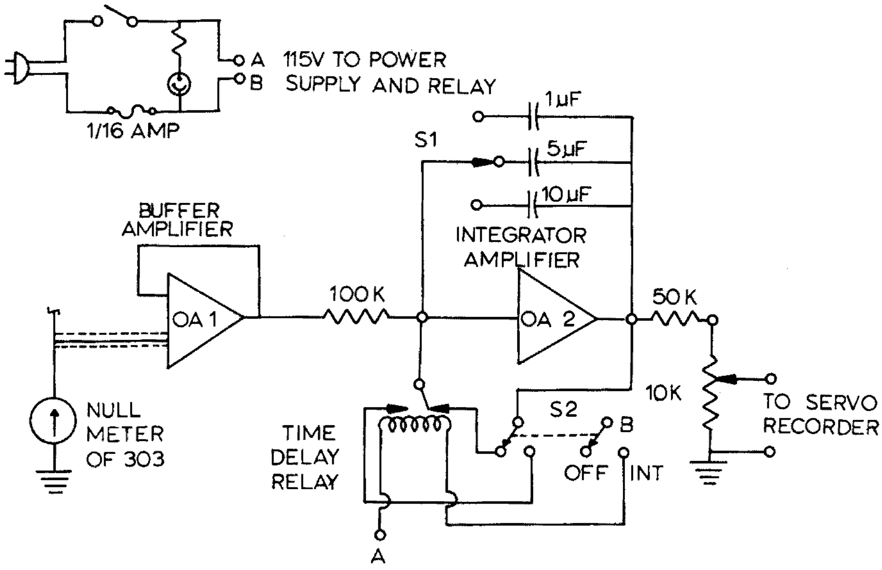

Fig. 1. Schematic diagram of analog integrator.

provides a selection of integration capacitor. Integration periods are initiated by throwing switch S2 to the INTEGRATE mode. This removes the shorting bypass from the integrating capacitor and applies a 115-V activating voltage to the time-delay relay (Guardian Adjustable Time Delay Relay, Allied Electronics, Chicago, Illinois). The solid-state relay has a repeatability of ±1%, a recycle time of 50 msec, and an adjustable time cycle of 10–60 sec set by a 15-turn miniature pot. At the end of the relay duty cycle, the integrating capacitor is shorted and the readout recorder returned to zero. To avoid diagram complexity, not shown is a double-pole, 4-position switch allowing the introduction of a gain of 10 balancing circuit to each amplifier along with a null meter for initial amplifier balance. Several different types of discrete component operational amplifiers (Analog Devices, Cambridge, Mass.) were used and are discussed later as to their advantages and limitations. All were powered by a Model 901 ±15V–40 mA power supply (Analog Devices). Balance controls were ten turn miniature helipots. Low noise resistors and low leakage capacitors were used for all integrator time constants.

All volumetric ware was class A. Working solutions were prepared in glass volumetric flasks and transferred to polyethylene bottles to minimize solution concentration changes caused by adsorption on container walls. Low p.p.b. solutions of magnesium were prepared fresh for each series of runs.

Reagents

Magnesium and lead working solutions were prepared by dilution of Fisher standard solutions (Fisher Scientific Company) with distilled water which was passed through a mixed-bed ion-exchange column.

RESULTS AND DISCUSSION

Analog integration in its simplest form involves no more than a RC low-pass filter[4]. If the RC time constant, T, is large relative to the repetition rate of input signal the output voltage taken across the capacitor is a linear ramp function. The integration circuit may be improved by placing the RC network in the negative feedback loop of a high gain operational amplifier, as is the case in Fig. 1. The output of the integrator is given by the expression:

$$e_0 = -\frac{1}{RC}\int_0^t e_{\text{in}}\,\mathrm{d}t \tag{1}$$

where e_0 is the output voltage after application of e_{in} input voltage for t sec with the time constant, $T = RC$, calculated in ohms × farads. The time constant thus determines the net "gain" of the integrator or e_0 sec^{-1}. Practical limitations on RC include input signal size, readout capacity, and amplifier drift. If a current source is to be integrated, such as the output of a photomultiplier tube, the input resistor is eliminated and expression (1) becomes:

$$e_0 = -\frac{1}{C}\int_0^t i_{\text{in}}\,\mathrm{d}t \tag{2}$$

Drift and offset in the operational amplifier may become serious instrumental limitations, depending on the magnitude of the information signal to be integrated.

An operational amplifier off balance which appears insignificant under normal use may become unacceptable when summed over a substantial integration period. It should be noted that the observation of integrator output with a grounded input represents a convenient final fine-balance method. Even if an amplifier is initially balanced exactly, it is possible that drift may occur during integration with subsequent error. Therefore, a series of solid state amplifiers were evaluated including a general purpose Model 105B, an FET input Model 141A, and a chopper stabilized Model 230J.

Amplifier drift

The low-cost, general-purpose amplifier exhibited a drift over 1-min integration times which became significant for very low absorbance samples. The FET input unit, recommended for integrator applications, had a greatly reduced drift factor and, upon repeated duplications of zero signal integration, showed high stability. As would be expected, the most suitable amplifier was the chopper-stabilized unit which continually corrected for any internal drift. However, the less expensive FET

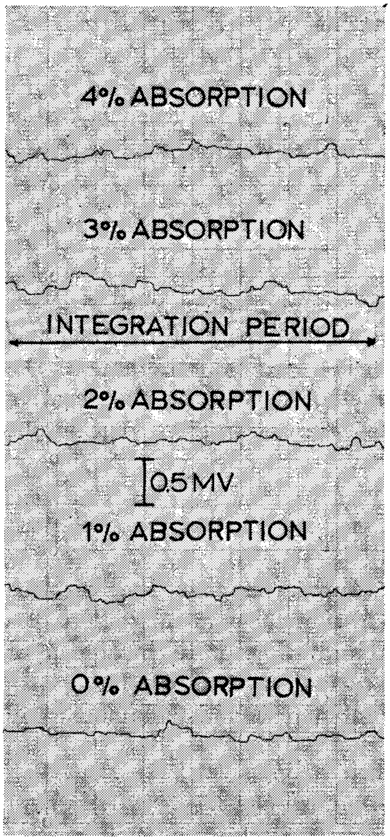

Fig. 2. Recorder display of short term noise associated with 0–4% absorption signals from the atomic absorption spectrometer, observed for a period of time equal to the integration period, 48 sec.

input amplifier would be satisfactory for most applications. A large number of comparison runs were made with each unit.

Effect of RC time constant

A large number of various time constants were used as well as different combinations of R and C to obtain a particular time constant. The value of the RC product is determined mainly by drift considerations and the magnitude of the signal input. Time constants ranging from 0.10 to 5.00 were evaluated for each amplifier under a variety of conditions. For this particular spectrometer-readout combination, an RC product of *ca.* 1 yielded the most satisfactory results when considering such factors as drift, stability, precision, and output signal magnitude.

Manufacturer's specification sheets are available[5] in selecting the resistance and capacitance values to use for a particular time constant to obtain minimum drift. The lower limit of R is determined by the minimum acceptable input impedance the integrator is to present to its signal input. This may be critical if an isolation amplifier is not used. C is then made as large as possible[5] within the impedance limitation of R. The 100 K input resistor did not visibly load the signal source upon elimination of the isolation amplifier, leaving a 10 μF value for C. It should be emphasized that other combinations were used and many of them quite satisfactorily. However, the 100 K–10 μF combination was judged to be most suitable.

Background noise

The intrinsic fluctuation of the output from the spectrometer was then examined. If the variations are indeed random, the use of an integrated readout would then be quite advantageous. Figure 2 shows tracings taken from the spectrometer output at various absorption signal levels ranging from 0 to 4%, demonstrating the short-term noise. These instantaneous signal and noise levels were then evaluated by a series of integrations to determine net signal and noise (or drift) after a specified integration period. Noise integrations at the several absorptions were made by backing the absorption signal off to zero initially and integrating the resulting fluctuations and drift. Table I shows signal-to-noise ratios for absorption signals by the direct readout method and by the integration method. The results suggested that low absorbance samples could be analyzed with much more confidence by integration techniques.

TABLE I

COMPARISON OF SIGNAL-TO-NOISE RATIOS FOR NORMAL *vs.* INTEGRATION READOUT
(Signal values in mV, integration period = 48 sec, Model 230J amplifier)

Per cent absorption	*Instantaneous*			*Integration*		
	Signal	*Noise*	*S/N*	*Signal*	*Noise*	*S/N*
0	—	0.2	—	—	0.3	—
1	1.7	0.2	8.5	21.6	0.3	72
2	3.4	0.3	10.1	46.4	0.4	116
3	5.3	0.3	17.5	68.2	0.5	136
4	7.1	0.3	23.7	93.5	0.5	187

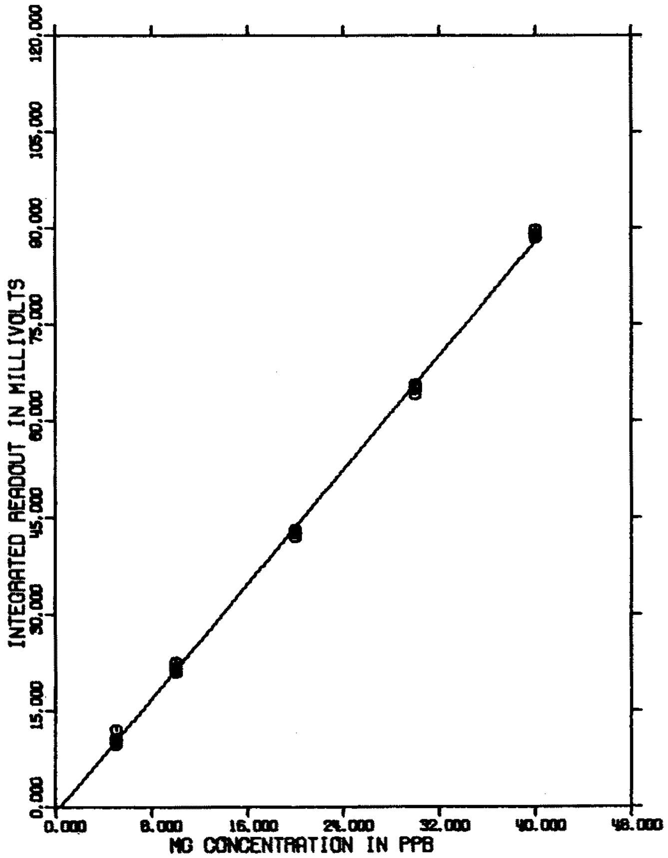

Fig. 3. Least squares curve fitting of integrated atomic absorption signal from magnesium working solutions. Wavelength = 2852 Å; integration period = 48 sec, Model 230J amplifier.

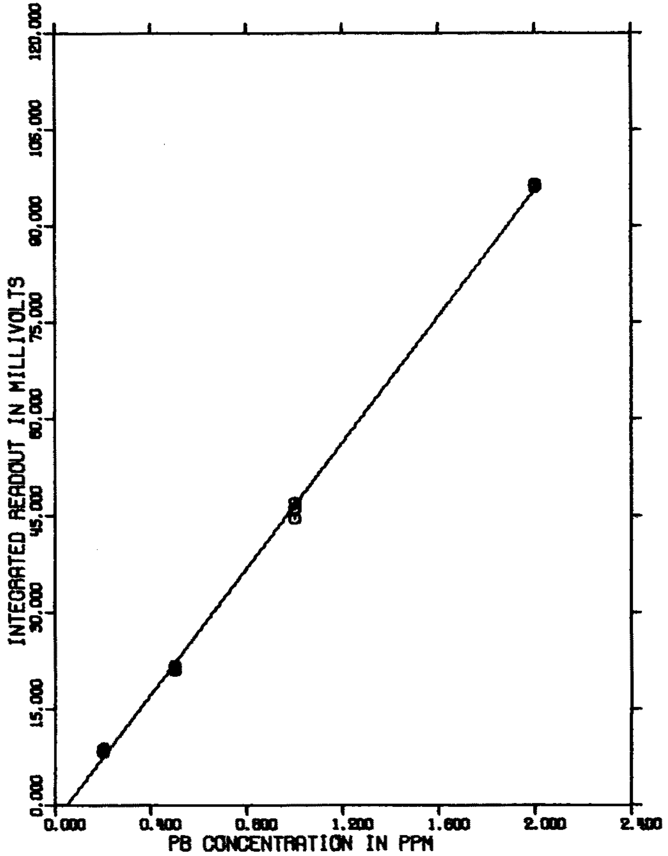

Fig. 4. Least squares curve fitting of integrated atomic absorption signal from lead working solutions. Wavelength = 2833 Å; integration period = 48 sec, Model 230J amplifier.

Reproducibility

For precision and reproducibility studies, magnesium and lead were selected as test elements owing to their wide applicability to atomic absorption and their considerable difference in absorption sensitivity. Table II shows the results of a series of representative runs for magnesium and lead of various concentrations. Data have been obtained which show better precision than those in Table II but slight instrumental variations can also create poorer reproducibility. The data shown here represent the precision obtainable with normal care to experimental parameters.

TABLE II

REPRODUCIBILITY OF INTEGRATION READOUT DATA FOR MAGNESIUM AND LEAD SOLUTIONS
(Integration period = 48 sec, Model 230J amplifier)

Concentration	*% Absorption*	*Integrated readout (mV)*	*Ave.*
Magnesium (p.p.b.)			
5	0.5	12.0, 9.8, 10.2	10.7
10	0.9	22.5, 21.0, 21.3	21.6
20	1.8	42.8, 42.0, 44.3	42.6
30	2.8	64.0, 65.0, 65.5	64.9
40	3.8	88.5, 89.7, 88.5	88.9
Lead (p.p.m.)			
0.5	0.8	8.7, 8.6, 9.0	8.8
1.0	1.8	19.0, 19.1, 19.5	19.2
2.0	3.5	39.5, 40.3, 39.5	39.7
4.0	7.2	87.0, 87.0, 87.0	87.0

A number of factors can affect the reproducibility. Since stability must be obtained over the entire integration period, it is important that the spectrometer and hollow-cathode tube be allowed to reach electronic and thermal equilibrium. The same is obviously true of the integration unit and readout recorder. Flame conditions must be carefully controlled and maintained. Samples should be allowed to aspirate for 10–15 sec before commencing integration, particularly for a very low percent absorption. The atomizer-burner should be flushed by aspirating distilled water briefly between samples. The zero absorption setting is best checked after each sample. It should be noted that these precautions are critical only for the very low absorbing solutions, but this is the area of greatest application for the integration techniques.

Working curves for the data in Table II are shown in Figs. 3 and 4. The readout is integrated percent absorption which, for low absorbing samples, is very nearly a linear response. A standard least squares curve fitting program was used for data analysis by a Burroughs B-5500 computer and subsequent display by a Calcomp plotter. A very slight amplifier off balance will produce plots with non-zero intercepts. This is usually not particularly critical if a sufficient number of standards are used to define the working curve. Figure 4 shows a series of plots for magnesium, illustrating the effect of different values of integrator capacitors and using a 750-K input resistor.

Other applications

The utility of the basic integrator unit is not limited to the application shown in this study. Other atomic absorption spectrometers could be used, including single-beam, non-null readout if provision is made for an opposing bias current into the summing point of the operational amplifier. Such measurements have been carried out on a modular single beam unit. The stability of the single-beam spectrometer is a critical factor.

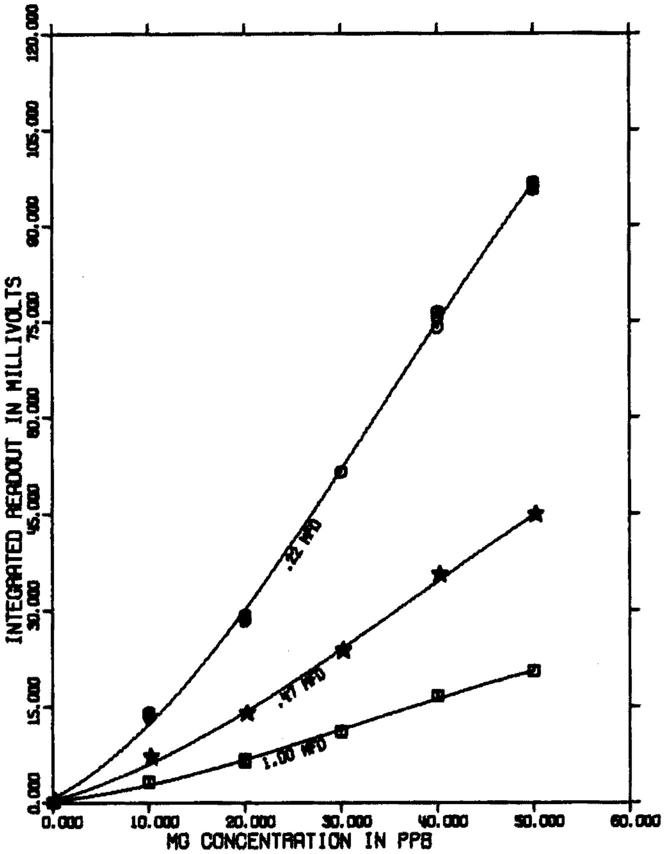

Fig. 5. Least squares curve fitting of integrated atomic absorption signal from magnesium working solutions showing the effect of changing the value of the integrator capacitor. Wavelength = 2852 Å; integration period = 60 sec. Model 141A amplifier.

Similar integrator units have been used in this laboratory to increase greatly the precision of flame emission analyses and are now used routinely. Other units have been used in instrumental analysis teaching laboratories to integrate the photomultiplier current output of an erratic d.c. arc discharge with a "direct reader" modification of a spectrograph, to integrate peak areas from the electrometer output of a gas chromatograph, and, by reversal of the resistor–capacitor combination, to provide direct first and second derivatives of automatic titration curves.

SUMMARY

An analog integrator is described and evaluated for the application of integrator techniques to low absorbing solutions by atomic absorption spectroscopy. Use of solid state operational amplifiers allows a stable, low drift integration of information signals to improve signal-to-noise ratios. The effects of experimental parameters are described and integration working curves are shown for solutions absorbing with 0–4% range.

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RADIOCHEMICAL SEPARATION OF GALLIUM BY AMALGAM EXCHANGE

R. R. RUCH
Analytical Chemistry Section, Illinois State Geological Survey, Urbana, Ill. 61801 (U.S.A.)

(Received May 26th, 1969)

Amalgam-exchange separation procedures have now been developed for many elements[1], but efforts to achieve isotopic exchange for gallium have been unsuccessful[2]. The purpose of this work was to demonstrate that isotopic exchange of Ga^0–Ga^{3+} can occur, and that such a technique is applicable in activation analysis. The initial exchange process may be expressed as follows:

$$\underset{\text{(excess)}}{Ga^0(Hg)} + {}^{72}Ga^{3+} \rightleftarrows {}^{72}Ga^0(Hg) + Ga^{3+}$$

where an aqueous solution of radioactive $^{72}Ga^{3+}$ is agitated with the metallic liquid amalgam, $Ga^0(Hg)$.

The second, or stripping, step may be expressed as follows:

$$^{72}Ga^0(Hg) \xrightarrow{\text{Oxidation}} {}^{72}Ga^{3+} + Hg$$

where the liquid amalgam is separated and selectively oxidized to remove the radioactive gallium.

Moorhead and Frame[3] recently published polarographic data indicating that reversible reduction of gallium can occur in acidic media of high ionic strength in the presence of thiocyanate. This information was used to devise a systematic approach to an optimum procedure, in which each necessary variable was evaluated.

EXPERIMENTAL

Reagents and apparatus

Analytical-reagent-grade chemicals were used throughout. A laboratory shaker (Eberback 6000 Reciprocating Model) was used at highest settings for all agitations. All radioactive counting was performed with a 3 × 3-in NaI detector with a Nuclear Chicago 3427 multichannel analyzer.

Amalgam preparation

A 0.3% gallium amalgam was prepared by adding 200 mg of gallium metal, previously cleaned by dilute nitric acid, to 5 ml of triple-distilled mercury. About 10 ml of 0.1 *M* citric acid was added and the mixture gently heated for 30–60 min until the gallium was visibly broken up and dissolved. The resulting liquid amalgam should appear completely homogenous and clean before use to prevent anomalous results.

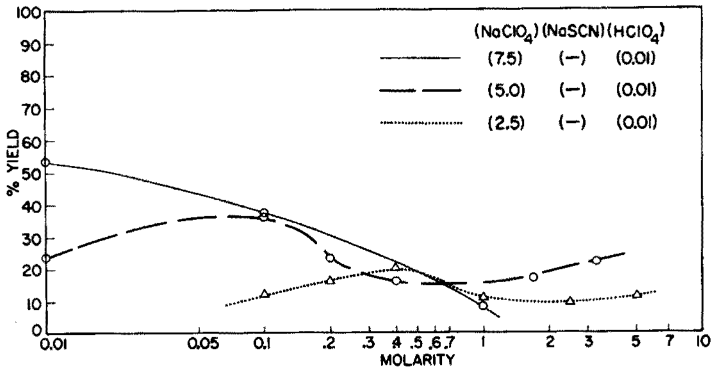

Fig. 1. Dependence of initial isotopic exchange upon sodium thiocyanate concentration at various concentrations of sodium perchlorate. The variable concentration in each case is designated by (—) in the key.

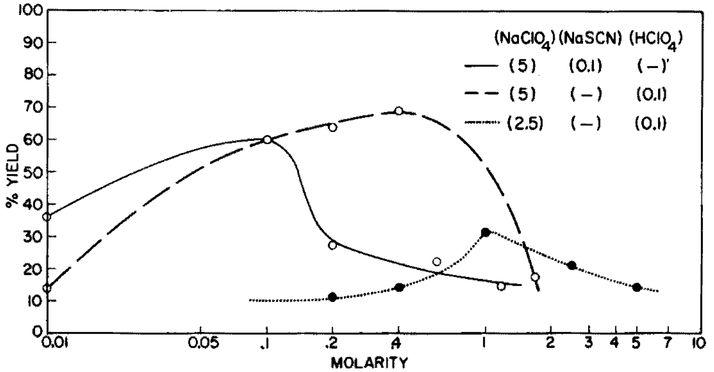

Fig. 2. Dependence of initial isotopic exchange upon perchloric acid and sodium thiocyanate concentration at various concentrations of sodium perchlorate. The variable concentration in each case is designated by (—) in the key.

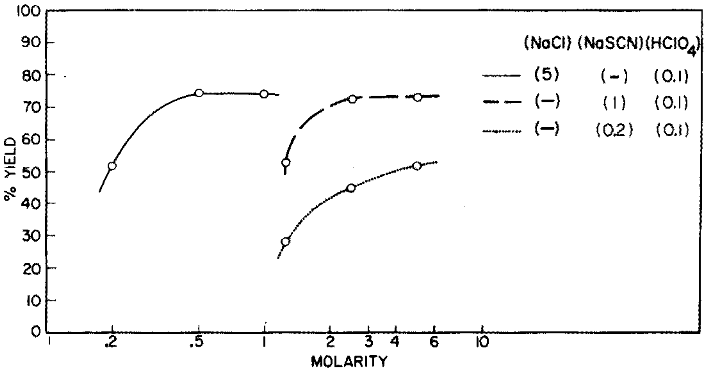

Fig. 3. Dependence of initial isotopic exchange upon sodium chloride and thiocyanate concentration at 0.1 M perchloric acid. The variable concentration in each case is designated by (—) in the key.

Preliminary studies

A series of experiments was conducted to find the optimum procedure. In general, the procedure employed was similar to that detailed for the sodium perchlorate or chloride system described below. In each series a variable was introduced, such as different concentrations of perchlorate, thiocyanate or perchloric acid, amount of gallium(III) in solution, volume of solution, volume of amalgam, or time of agitation.

Procedures

Perchlorate system. A 0.25-ml aliquot of the gallium amalgam ($\sim$10 mg Ga^0) was transferred to a small vial containing 5 ml of a solution made up of 5 *M* in sodium perchlorate, 0.2 *M* in sodium thiocyanate, 0.1 *M* in perchloric acid, and a trace of $^{72}Ga^{3+}$. The mixture was purged with nitrogen for about 30 sec, and the vial was capped and agitated on a mechanical shaker for 30 min. The amalgam was then physically removed from the solution by replicate gravity transfers through large separatory funnels filled with distilled water.

The amalgam containing the exchanged radioactive $^{72}Ga^0$ was then added to 5 ml of 2 *M* nitric acid in another vial, which was capped and agitated for 1 h. The resulting solution was counted for $^{72}Ga^{3+}$, which had been quantitatively stripped from the amalgam.

Chloride system. This procedure was identical with the sodium perchlorate procedure, but the initial solution was 5 *M* in sodium chloride, 0.5 *M* in sodium thiocyanate, and 0.1 *M* in perchloric acid.

RESULTS

Results of preliminary studies

Figures 1 and 2 indicate the trends observed when sodium perchlorate or thiocyanate or perchloric acid concentrations were varied. At lower sodium thiocyanate molarities, increased sodium perchlorate concentration tended to promote better exchange yields. As the molarity of sodium thiocyanate increased, however, it controlled the exchange, which went through a maximum, decreased, then slightly rose again. Acid concentration (Fig. 2) had the general effect of promoting maximum yields near 0.1 *M* perchloric acid and then markedly decreasing the yield at higher levels.

A similar trend took place when sodium chloride was substituted for sodium perchlorate (Fig. 3). Isotopic exchange increased but levelled off when either chloride or thiocyanate concentrations were increased and while the perchloric acid was held constant at 0.1 *M*.

In the procedure described for the sodium perchlorate system, the amount of gallium(III) present in the 5 ml of solution was varied from 0.01, 0.23, to 3.2 mg, resulting in initial isotopic exchange yields of 95%, 64%, and 43%, respectively, which indicated major dependence. Similarly, when the solution volume was altered, initial isotopic exchange yields were 85%, 64%, and 41%, respectively, for 5, 10, and 20 ml, showing critical dependence.

The optimum time of shaking was determined by observing initial isotopic exchange yields of the sodium perchlorate system as a function of time agitated. The

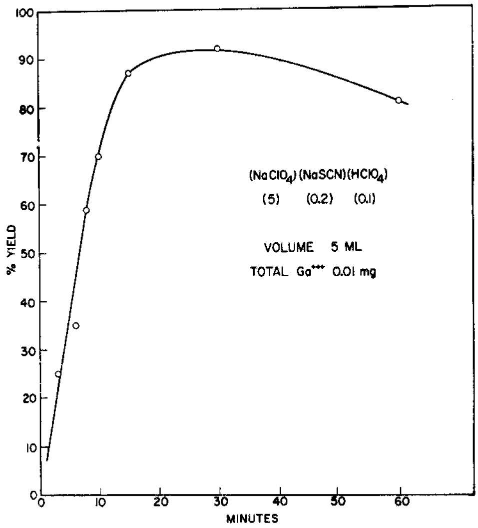

Fig. 4. Dependence of initial isotopic exchange upon time of agitation. All concentrations are molar.

TABLE I

COMBINED EXCHANGE YIELDS

Conditions				*% Yield*[a]
$NaClO_4$	$NaSCN$	$HClO_4$	Ga^{3+}/5 ml	
5 *M*	0.2 *M*	0.1 *M*	0.03 mg	90 ± 4
$NaCl$	$NaSCN$	$HClO_4$	Ga^{3+}/5 ml	
5 *M*	0.5 *M*	0.1 *M*	0.2 mg	75 ± 4
5 *M*	0.2 *M*	0.1 *M*	0.2 mg	49 ± 5

[a] Average of 5 determinations and standard deviation.

TABLE II

COMBINED DECONTAMINATION YIELDS[a]

Element (ca. 1 mg)	*Average of duplicate determinations (%)*
$^{24}Na^{+}$	<0.002
$^{89}Sr^{2+}$	<0.004
$^{82}Br^{-}$	<0.0005
$^{56}Mn^{2+}$	<0.003
$^{69}Zn^{2+}$	<0.009
$^{51}Cr^{3+}$	<0.003
$^{60}Co^{2+}$	<0.005
$^{140}La^{3+}$	0.02
$^{198}Au^{3+}$	0.45
$^{187}W^{5+}$	1.6
$^{122}Sb^{3+}$	16

[a] $NaClO_4$ procedure used.

results in Fig. 4 indicate 30 min as a maximum, with yield dropping off afterwards, possibly because oxidization of gallium from the amalgam competes with the exchange reaction. Studies of the back-exchange, or stripping, with 2 *M* nitric acid indicated that at least 1 h was required for complete removal under the conditions employed.

Results of optimized procedures

The combined initial isotopic exchange and stripping yields of the two optimum procedures are shown in Table I. The sodium perchlorate system gives yields of 90% with fair reproducibility. The sodium chloride system combined exchange yields of 75%, although lower, are reproducible.

Combined exchange yields for a series of possible 1-mg contaminants are shown in Table II. Of the isotopes tested, with the exception of tungstate and antimony(III), most demonstrate good decontamination.

DISCUSSION

Highly concentrated solutions of sodium perchlorate or chloride with sodium thiocyanate can effect appreciable isotopic exchange in the Ga^{3+}–Ga^0 system. A $Ga(SCN)_4^-$ complex probably promotes the exchange mechanism[3]. Such a technique can approach quantitative exchange, with good decontamination, making it useful in activation analysis for the determination of trace amounts of gallium.

A possible explanation for non-quantitative yields is that the rate of oxidation of metallic gallium from the amalgam is *not* insignificant compared to the kinetics of isotopic exchange on the amalgam–solution interface.

The experimental variables demand precise duplication of conditions for both sample and standards to obtain minimum differences in yield for replicate situations or for yield determinations.

The interest of S. M. KIM of the Illinois State Geological Survey staff in this work and his comments during its progress have been most stimulating. The cooperation of the University of Illinois Reactor Facility in producing the various isotopes utilized also is gratefully acknowledged.

SUMMARY

An amalgam-exchange separation of radioactive gallium from a number of interfering radioisotopes has been developed. A dilute (*ca.* 0.3%) gallium amalgam is agitated with a slightly acidic solution of $^{72}Ga^{3+}$ containing concentrations of sodium thiocyanate and either perchlorate or chloride. The amalgam is then removed and the radioactive gallium stripped by agitation with dilute nitric acid. The combined exchange yield of the perchlorate–thiocyanate system is $90 \pm 4\%$ and that of the chloride–thiocyanate system is $75 \pm 4\%$. Decontamination yields of most of the 11 interfering isotopes studied were less than 0.02%. The technique is applicable for use with activation analysis for the determination of trace amounts of gallium.

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THE X-RAY SPECTROMETRIC DETERMINATION OF URANIUM AND PLUTONIUM IN SOLUTIONS OF SPENT NUCLEAR FUELS*

P. A. PELLA** AND A. V. BAECKMANN
Institut für Radiochemie, Kernforschungszentrum, Karlsruhe (Federal Republic of Germany)
(Received May 12th, 1969)

X-Ray spectrometric analyses for uranium and plutonium in aqueous and organic solutions have previously been reported[1-3]. Two recent publications cite a comprehensive bibliography of pertinent applications[1,2]. However, little or no work has been described concerning the direct measurement of these elements in β,γ-radioactive solutions of spent nuclear fuels at or above the 1-Ci level.

There are three points in the nuclear fuel cycle where the flow of fissile material can be controlled by direct chemical methods. The first point is at the input of a reprocessing plant where the fuel elements are dissolved (dissolver solutions). In addition to the various fission product elements and possibly some dissolved cladding present, the level of β,γ-radioactivity in these solutions is relatively high. The second point is at the output of the reprocessing plant where the fissile material is essentially free from other elements and at a relatively low β,γ-activity level. The third is at that point in the fabrication plant where the fissile material is filled into the cladding. Here the fissile material is in the form of powders or pellets of pure or mixed oxides.

The X-ray spectrometric method is specific, tamper-proof, and could in principle be highly automated. For these reasons, its application at all three points in the cycle could prove valuable in controlling the fissile material balance, especially in connection with the safeguarding of nuclear fuel.

The principal areas investigated include the determination of the effects of other elements present, the level of β,γ-radioactivity that could be safely handled, and the use of shielding in order to minimize the detector background. In addition plutonium was measured in the presence of a large excess of uranium because the uranium-to-plutonium ratio in dissolver solutions is often high.

To obviate the need for independent verification of the results, the uranium and plutonium were removed from actual dissolver solutions by extraction with tri-*n*-butyl phosphate (TBP). Then known amounts of uranium and plutonium were added and determined with thorium as an internal standard.

EXPERIMENTAL

The following spectrometer characteristics were considered essential for the

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* Presented at the meeting of the GDCh-Fachgruppe "Analytische Chemie" in Freiburg (Germany), April 1969.

** Work done while on leave from the National Bureau of Standards, Washington, D.C. Present address: National Bureau of Standards, Washington, D.C.

successful application of this technique. First, an instrument with a high resolution is needed, because of the high scattering power of solutions. Secondly, the X-ray tube should have a much greater intensity than the γ-radiation intensity from the sample. Thirdly, the analyzer crystal should have a reflecting angle as large as possible in order to optimize the ratio of the detected fluorescent intensity to the detected γ-radiation. In addition necessary modifications must include a sample changer which provides adequate shielding to protect the operator and can be adapted for use in a glove box necessary for handling plutonium-containing materials.

Apparatus

The X-ray equipment consisted of a Siemens Sequential X-Ray Spectrometer SRS 1 unit, a NaI(Tl) scintillation detector, and a LiF analyzer crystal (section 110), $2d = 2.84$ Å. The AG 61-chromium and AG 61-tungsten target X-ray tubes were employed and the operating conditions were 60 kV and 30 mA, and 55 kV and 32 mA, respectively.

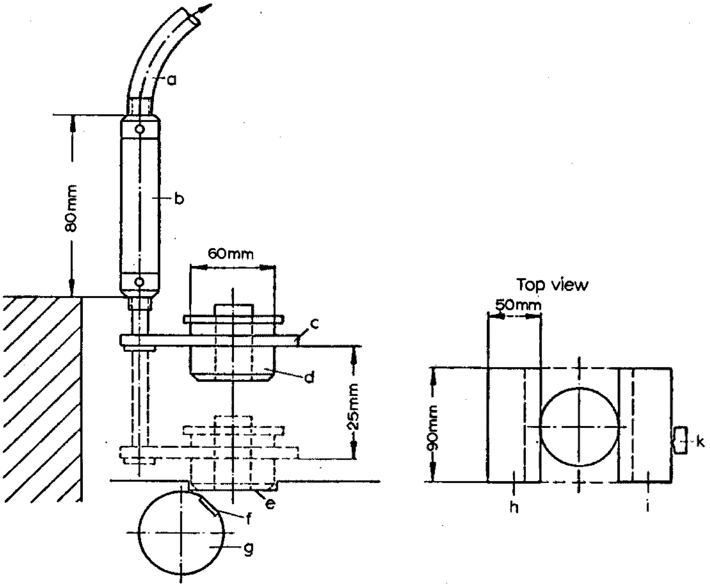

Fig. 1. Schematic diagram of the manually operated sample changer. (a) Tygon tubing to the compressed-air source; (b) pneumatic cylinder; (c) aluminum support for the sample container; (d) sample container; (e) beryllium disc (94 mg/cm^2) placed over a hole cut in the bottom of the glove box; (f) X-ray tube window; (g) X-ray tube; (h, i) lead shields shown in top view over the Be disc e; (k) switch for operating the piston of the pneumatic cylinder.

The original sample changer was replaced with a manually operated one as illustrated in Fig. 1. Two lead shields (h, i) shown on the right in the figure are operated by a gear mechanism which is connected to a knob. Rotation of the knob causes the lead shields to open and close directly over the beryllium disc (e). When the lead shields are fully opened, shield i makes contact with switch k. The compressed-air driven piston of pneumatic cylinder b drives downward positioning the sample container directly over the X-ray window as shown by the dotted lines in the figure.

Conversely, the closing of the lead shields releases switch k and the piston drives upward returning the sample container to its previous position. An obvious advantage of such a system is that the sample can be changed without interruption of the high-voltage power supply. The entire sample changer is enclosed by a 5-cm thick lead chamber which serves to protect against primary X-ray radiation and also from nuclear radiation from the sample itself. Finally, the chamber is enclosed by a glove box. Two safety features include a warning lamp indicating when the lead shields (h, i) are opened and a cut-off switch for the high-voltage power supply. A photograph of the modified spectrometer is shown in Fig. 2.

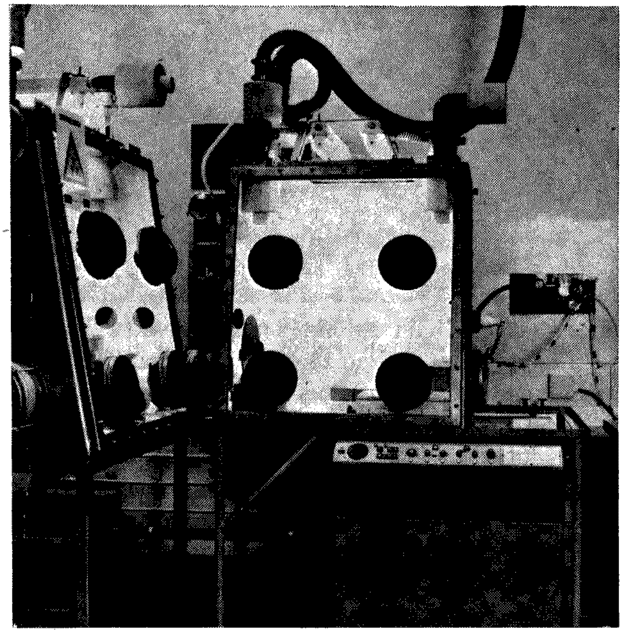

Fig. 2. Photograph of the modified Spectrometer Unit.

Preparation and treatment of dissolver solutions

Three dissolver solutions were employed from UO_2 fuel elements irradiated in the FR-2 reactor at Karlsruhe. Solution I was obtained by the dissolution of fuel element NC-3 (burn-up = 1.3%, enriched to 1.5%) in concentrated nitric acid. This solution was diluted to about 8 *M* in nitric acid and extracted seven times with equal portions of 35% tributyl phosphate (TBP) in dodecane and washed with 10 ml of dodecane. The organic phase was then discarded. Measurement of the absolute β,γ-radioactivity in the extracted dissolver solution gave a result of 130 mCi/g of solution with an accuracy of $\pm 10\%$.

Solutions II and III were obtained by dissolution of two different portions of a test element of FR-2 (burn-up = 4.5%, enriched to 11.5%) in nitric acid and similarly extracted with TBP and washed with dodecane. To 25 ml of the extracted solution III was added about 900 mCi of cesium-137. The absolute β,γ-activities measured for solutions II and III were 175 and 332 mCi/g $\pm 10\%$, respectively. Examination of the dissolver solutions before and after extraction with a Li-drifted Ge detector showed that appreciable amounts of zirconium–niobium-95 were extracted; otherwise, there was no significant change in the fission product composition.

Stock solutions

All chemicals were of A. R. grade. Stock solutions of uranium and plutonium were prepared by dissolving U_3O_8 and PuO_2 in concentrated nitric acid and diluting to volume with distilled water. The final acid concentration in these solutions was about 3 *M*. The plutonium concentration was verified to an accuracy of better than 0.5% by constant potential coulometry and redox titration with cerium(IV). The thorium internal standard solution was prepared by dissolving thorium nitrate in 3 *M* nitric acid and diluting to volume.

Procedure

To 50-ml polyethylene flasks containing known weights of uranium and thorium stock solutions, or plutonium and thorium stock solutions plus appropriate amounts of solid uranyl nitrate hexahydrate, was added about 3–4 ml of extracted dissolver solution. This solution (5–6 ml) was weighed and then decanted into a poly cylinder (20 mm in diameter × 30 mm in height), the bottom of which was a 0.5-mm thick poly window. The sample cylinder was covered with a snug-fitting poly cap and loaded into the sample container.

The intensity of the $L\alpha_1$ lines was measured for 1 min in most cases at $2\,\theta$ values of 35.540° for plutonium, 37.370° for uranium, and 39.280° for thorium. The background intensity measurements were made at 35.040°, 36.540°, 38.870°, 39.030°, and 40.080°. The intensity ratios, *i.e.* $I_{U,Pu}/I_{Th}$, were computed and compared with the ratios from appropriate standard solutions which were prepared in an identical manner as the above except that 5 *M* nitric acid was substituted for the dissolver solutions.

RESULTS AND DISCUSSION

To minimize the contribution of γ-radiation from the sample to the detector background, lead shielding was used within and on the side of the spectrometer casing as shown in Fig. 3. The relative effectiveness of each shield can be judged from Table I. It can be seen that the three shields together reduce the detector background by a factor of about four. The location of shields 5 and 6 was convenient as well as effective because they are not stationary but move with changing $2\,\theta$ angle.

The results of the determination of uranium in dissolver solution I are tabulated in Table II. The detector background from the γ-radiation alone was about 1400 counts/min and is 7–10% of the background intensities with the chromium X-ray tube. The concentration range investigated represents the working range normally encountered in this laboratory. Since the uranium concentration in actual dissolver solutions is much higher, dilution to the desired working range presents no problem. The relative standard deviation of a single measurement computed from the random counting error only was 1.0%, and the value obtained from 25 measurements on a standard solution was 1.1%. It can be seen from the Table that the relative error of these measurements compares well with the precision of the method.

In Table III are shown the results of the plutonium determination made in

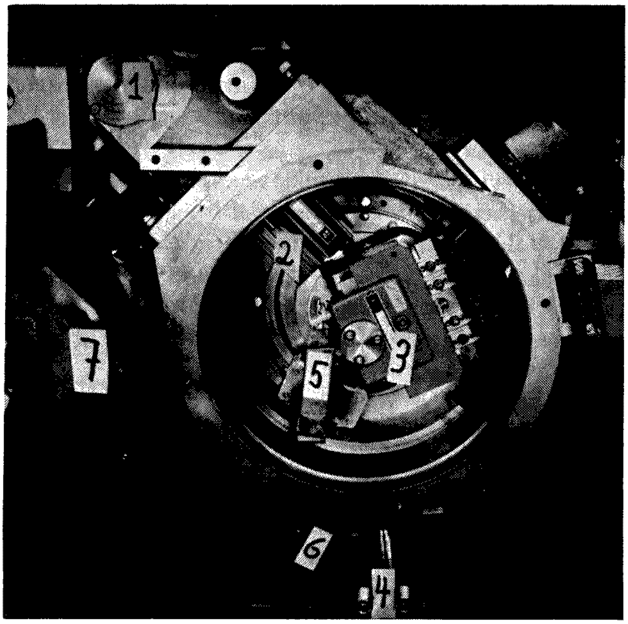

Fig. 3. Photograph of the Goniometer Unit. (1) Indicates the position of the sample which lies just above this point; (2) Soller slits; (3) crystal changer with LiF (110) crystal; (4) NaI(Tl) scintillation detector; (5) lead shield (20 mm × 60 mm × 75 mm) mounted on the proportional counter support; (6) lead shield (20 mm × 80 mm × 60 mm) so mounted as to move with the detector; (7) lead shield made with 50 mm thick lead bricks.

TABLE I

THE EFFECT OF LEAD SHIELDS ON THE DETECTOR BACKGROUND

Shield no.	*Counts/min (Integral)*	*Counts/min (Differential)*[a]
None	315,000	5,730
7	245,000	4,460
5	132,000	2,410
5 + 7	102,000	1,730
5 + 6 + 7	67,980	1,400

[a] The single channel was set at a base level of 9.4 V and a channel width of 6.0 V.

the presence of an excess of uranium. Dissolver solutions II and III were used in these samples. The detector background from the γ-radiation was 1900 and 2800 counts/min, respectively. These values still represent a range from only 4 to 10% of the background intensities with either the chromium or the tungsten target X-ray tubes. It was noted that appreciable amounts of the strong γ-emitters ^{95}Zr/Nb were extracted from the dissolver solutions. Therefore an amount of cesium-137 equivalent to the amount of ^{95}Zr/Nb originally present was added to dissolver solution III in order to simulate the effect of these nuclides on the detector background. In comparing the results from the two dissolver solutions in Table III, no great difference was observed.

In the plutonium analysis, the intensity ratio I_{Pu}/I_{Th} was found to be de-

TABLE II

DETERMINATION OF URANIUM IN DISSOLVER SOLUTION

U present[a]	*U found*	*Relative error (%)*	*β,γ-Radioactivity (mCi fission prod./sample)*
17.98	17.89	−0.5	679
11.47	11.33	−1.2	720
4.827	4.819	−0.2	693
2.055	2.051	−0.2	679
1.049	1.038	−1.0	670
0.490	0.493	+0.7	693
0.236	0.238	+0.6	720
0.0922	0.0905	−1.9	680
0.0491[b]	0.0500	+1.8	680
0.0491	0.0516	+5.2	680
0.0491	0.0480	−2.2	680

[a] All concentrations are expressed in mg of U or Pu per g of solution.
[b] The relative standard deviation of a single measurement at this concentration was 3.0%. The counting time was 5 min.

TABLE III

DETERMINATION OF PLUTONIUM

Pu present[a]	*Pu found*	*Relative error (%)*	*U present*	*Ratio U/Pu*	*β,γ-Radioactivity (mCi/sample)*
Dissolver solution II					
1.0584	1.0521	−0.6	0	—	718
0.9932	0.9952	+0.2	0	—	667
0.8873	0.9013	+1.6	19.5	22	659
0.9351	0.9392	+0.4	40.0	43	843
0.8437	0.8441	+0.04	82.4	98	782
0.6990	0.7101	+1.6	138	198	840
0.6046[b]	0.5959	−1.4	184	302	791
Dissolver solution III					
1.2394	1.2675	+2.3	0	—	1332
1.1387	1.1201	−1.6	20.0	18	1284
1.0226	1.0402	+1.7	44.8	44	1256
1.0974	1.0754	−2.0	81.7	74	1115

[a] All concentrations are expressed in mg of U or Pu per g of solution.
[b] This sample was counted for 2 min.

pendent on the uranium concentration and decreased to 30% of the initial value at 184 mg U/g. Hence it is necessary for accuracy to prepare standards containing uranium with approximately the same concentration as the dissolver solutions. The difference in the uranium concentration between the present standards and the dissolver solutions did not exceed ±10%.

Examination of the X-ray spectra of the dissolver solutions in the 2θ region of interest revealed the presence of strontium which is produced in high yields as a fission product. Furthermore, the Sr Kα line at 35.860° is very close to the Pu Lα line at 35.540°. The effect of increasing strontium concentration on the $I_{\mathrm{Pu}}/I_{\mathrm{Th}}$ ratio was investigated. Only a small effect was observed until the strontium was four times the plutonium concentration. This resulted in an 8% increase in the I_{Pu}/I_{Th} ratio. In practice, the presence of strontium should cause no interference. This is because the plutonium will normally be greater than the strontium concentration in those dissolver solutions where the plutonium concentration is large enough to be measured by this method.

Actual dissolver solutions were analyzed for uranium in the 20–70 mg/ml range and compared with analyses by a mass-spectrometric isotope-dilution method performed at the Eurochemic company, Mol, Belgium. The β,γ-activity of these solutions was much lower, however, than the levels investigated in this work. Comparison of the mean values between the two laboratories indicated agreement within ±0.2% and demonstrated the absence of any systematic error.

CONCLUSION

From the results it is evident that the X-ray spectrometric method could be used to analyze uranium and plutonium in highly β,γ-radioactive dissolver solutions. Simultaneous analysis of these elements should be possible in dissolver solutions obtained from UO_2/PuO_2 fuel elements or from fuels where the plutonium concentration is greater than 0.3% of the uranium concentration. The sample with the highest β,γ-radioactivity level available which could be safely handled in this work contained about 1330 mCi of fission products. It was shown that the detector background even at this level could be reduced to a relatively low value by means of effective shielding. Preliminary experiments indicated that it was possible to measure solutions with levels up to 2 Ci without seriously increasing the detector background.

Further efforts are now under way to automate the entire measurement system. These include the sampling, sample treatment, and the calculation by computer of the analytical results.

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SUMMARY

X-Ray spectrometry is applied to the determination of uranium and plutonium in dissolver solutions containing fission-product activities up to 1330 mCi. Uranium was measured in the concentration range 0.05–18 mg/g of solution and plutonium in the range 0.6–1.2 mg/g of solution with thorium as an internal standard. Plutonium was determined in the presence of a large excess of uranium and solutions with U/Pu ratios up to 300 were measured. The relative standard deviation of a single measurement was 1.0–3.0% over the concentration ranges investigated. The effect of direct γ-radiation from the sample on the detector background was demonstrated and minimized by means of lead shielding. It is suggested that samples with radioactivity levels up to 2 Ci could be measured safely and without seriously increasing the detector background. The application of this method at certain points in the nuclear fuel cycle may be important in the safeguarding of nuclear fuel.

RÉSUMÉ

La spectrométrie aux rayons-X est appliquée au dosage de l'uranium et du plutonium dans des solutions présentant des activités de produit de fission allant jusqu'à 1330 mCi. L'uranium est mesuré à des concentrations de 0.05 à 18 mg/g de solution et le plutonium de 0.6 à 1.2 mg/g de solution, en utilisant le thorium comme étalon interne. Le plutonium peut être dosé en présence d'un grand excès d'uranium; des solutions dans un rapport U/Pu allant jusqu'à 300 ont été mesurées. La déviation standard d'une simple mesure est de 1.0 à 3.0%. L'influence de la radiation γ directe de l'échantillon sur le "background" du détecteur est démontrée et diminuée à l'aide de plomb. L'application de cette méthode est importante pour le contrôle de sécurité d'un fuel nucléaire.

ZUSAMMENFASSUNG

Die Röntgenspektralanalyse wird für die Bestimmung von Uran und Plutonium in Lösungen mit Spaltproduktaktivitäten bis zu 1330 mCi verwendet. Uran wurde im Konzentrationsbereich von 0.05–18 mg/g Lösung und Plutonium von 0.6–1.2 mg/g Lösung unter Verwendung von Thorium als inneren Standard bestimmt. Plutonium wurde in Gegenwart eines grossen Überschusses von Uran und in Lösungen mit einem U/Pu-Verhältnis bis zu 300 bestimmt. Die relative Standardabweichung betrug in dem untersuchten Konzentrationsbereich 1.0–3%. Der Einfluss der γ-Strahlung der Probe auf den Detektor-Untergrund konnte durch Verwendung einer Bleiabschirmung verringert werden. Es wird angenommen, dass Proben bis zu einer Radioaktivität von 2 Ci untersucht werden können ohne ernsthaftes Ansteigen des Detektoruntergrundes. Die Anwendung dieser Methode beim Kernbrennstoff-Zyklus ist für die Sicherheitsüberwachung von Bedeutung.

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THE UTILISATION OF FUEL-RICH FLAMES AS SULPHUR DETECTORS*

W. E. RUPPRECHT AND T. R. PHILLIPS
The Gas Council, Midlands Research Station, Wharf Lane, Solihull, Warwickshire (England)

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Certain inorganic radicals produce characteristic band spectra in flames. These have been described and tabulated in several publications[1-3]. When sulphur compounds are introduced into flames, the spectra emitted depend on the experimental conditions—whether the flame is premixed or diffusion, the nature of the combustant, the fuel/oxygen ratio, and the type of sulphur compound introduced[4,5]. However, in diffusion flames or when the mixture being burnt is deficient in oxygen, the S_2 spectrum may be observed at some point within the flame, in addition to any other spectrum which may be present. It is most readily seen in hydrogen flames; if hydrocarbons are present in any quantity and a yellow flame is produced by the luminescence of carbon particles, the sulphur spectrum is obscured. In enclosed premixed flames, the appearance of the violet-blue colouration associated with the S_2 spectrum is a good indication that the flame is deficient in oxygen. When town gas used to contain a higher concentration of sulphur compounds than it now has, this phenomenon was used by gas engineers to control the air/gas ratios in premixed burners[6-8].

Several applications of the flame photometric detection and determination of sulphur compounds have been reported. A German patent describes an enclosed cooled burner system suitable for the determination of sulphur (and phosphorus) compounds in air[9]. CRIDER[10] and DAGNALL *et al.*[11] have both used the emission from a hydrogen flame for the estimation of oxides of sulphur and sulphuric acid aerosols. BRODY AND CHANEY[12] developed a gas chromatographic hydrogen flame detector, and in a commercially available form which has been developed, the flame detector is combined with an ionisation detector[13].

The need for the continuous determination of total sulphur in petroleum feedstocks and natural gas is well known, particularly in catalytic reforming processes. Preliminary experiments with an apparatus similar to the type described by BRODY AND CHANEY showed that continuous introduction of hydrocarbon into a flame did not produce a satisfactory emission and that it could only be successfully used when attached to a chromatograph as originally described. Following an investigation of the variables involved, a double burner has been devised which does allow continuous measurement to be made. Some applications of this and the gas chromatographic detector have been investigated.

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EXPERIMENTAL

Burner design

Initially, experiments were made to compare the emission from different burners when samples of a gas containing sulphur in the form of hydrogen sulphide or sulphur dioxide were introduced into the burner gas supply. Hydrogen was used as the fuel gas, and the burners were successively mounted in the sample holder of the fluorescence attachment of an Optica CF4 double-beam recording spectrophotometer. Initially, the emission spectrum from a flame burning within an open-ended tube was obtained and found to correspond to that reported[2,3] for S_2 (Fig. 1). Thereafter, the emission intensity at 394 nm was recorded while conditions of flow, burner design and injected gases were altered.

Several burner designs, utilising diffusion, premixed and nozzle-mixed flames were tried, and best results were obtained when the supply of oxygen was controlled by enclosing the burner so that atmospheric oxygen did not have access to the flame. The most successful version is shown in Fig. 2; it is a nozzle-mixed burner contained in a clear quartz sleeve. Maximum emission was observed when the flow rates were within the following limits: hydrogen 310–480 ml/min, oxygen 15–40 ml/min. Shielding the lower part of the flame reduced the continuous background emission, and a slightly higher response was observed when the sulphur compounds added were premixed with the hydrogen rather than with the oxygen. To test the response of different com-

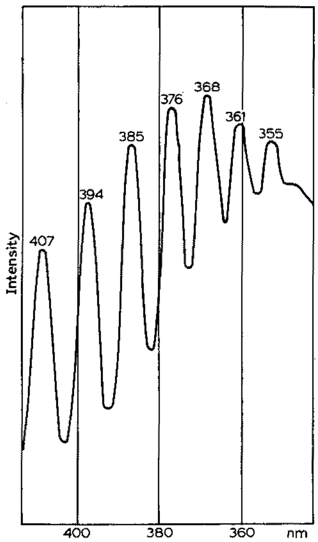

Fig. 1. S_2 spectrum from hydrogen flame.

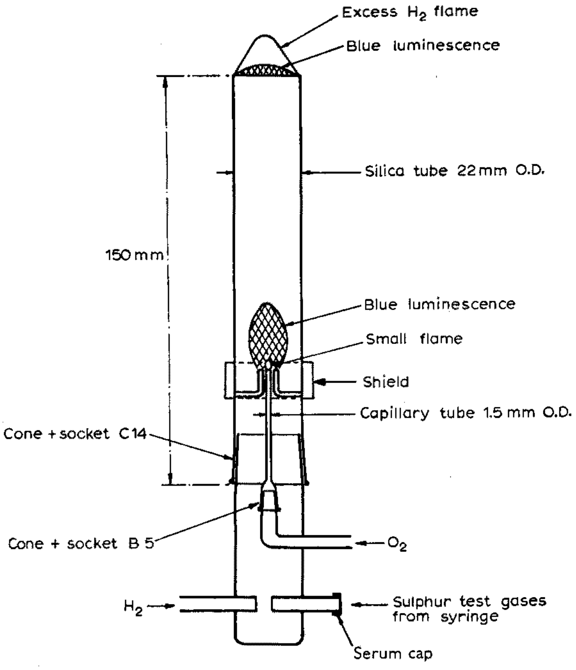

Fig. 2. Nozzle-mixed burner.

TABLE I

RESPONSE PRODUCED BY SOME SULPHUR COMPOUNDS IN A HYDROGEN FLAME

Sulphur compound	*Peak area measured (cm²)*	*Sulphur compound*	*Peak area measured (cm²)*
H_2S	4.10	$(CH_3)_3CH\ CH_2SH$	4.12
	3.75		4.31
	4.23		4.00
COS	3.96	$[(CH_3)_3C]_2S$	3.62
	3.90		3.51
	4.13		3.10
SO_2	4.20	CS_2	4.07
	3.80		4.31
	3.96		
CH_3SH	4.26	C_4H_4S	3.99
	4.13		4.30
	4.10		
$(CH_3)_2S$	3.83	$(CH_2)_4S$	4.12
	3.94		4.29
	4.20		4.20

pounds, a serum cap was fitted to the hydrogen line and gas samples were injected with a syringe. The sulphur compounds shown in Table I were mixed with nitrogen to give samples containing 50 p.p.m. (v/v) sulphur and 1-ml aliquots were injected. The resulting emissions were recorded on a chart and the peak areas determined by triangulation. From the Table it may be seen that with the exception of *tert.*-butyl sulphide, the response was approximately independent of the compound. The anomaly was thought to be due to the impurity of the reagent. The variations observed between samples were probably due to the non-linearity of the response to sulphur concentration.

The relation between sulphur concentration and detector response

For subsequent experiments, the burner was mounted in a system similar to that described by BRODY AND CHANEY[12]; light from the burner passed through a dielectric interference filter (Baird Atomic S/UV, bandwidth at half-peak—5 nm) with peak transmission of 25% at 394 nm, before falling on an end-viewing photomultiplier tube (EMI 9524B). The tube was powered by HT batteries and the output displayed on a strip chart recorder. The burner assembly was contained in a light-proof housing.

Samples of different concentrations of carbon disulphide in nitrogen were injected into the hydrogen flow supplying the detector, and peak heights were recorded. As found by others[10,11], the peak heights were not a linear function of concentration; over a limited range they were approximately proportional to the square of concentration but if the concentration was further increased, little increase in response was obtained.

Figure 3 shows the result obtained when a large amount of sulphur (10 ml of N_2 containing 1000 p.p.m. CS_2) was injected onto a column of 20% squalane on Embacel, placed upstream of the burner. This amount overloaded the column and a long, tailing peak was produced with inflection points showing discontinuities in the response. This emphasised that the response was not only non-linear, but irregular as well.

It was therefore evident that equal peak areas could not be expected from equal quantities of sulphur in different compounds if these were eluted at different times from a chromatograph column, because the effects of peak broadening would give different concentrations of sulphur in the carrier gas. Only in the absence of a column (as in the earlier experiments) when the peak shape was fairly constant could a constant response be obtained.

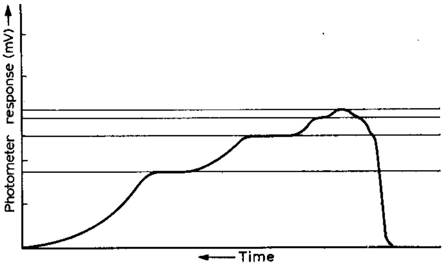

Fig. 3. Elution of high concentration of carbon disulphide from a chromatograph, showing discontinuities in detector sensitivity.

Calibration for each component is therefore necessary if a mixture is to be analysed chromatographically and because of the non-linearity of the response, peak height is a satisfactory measure of the response.

Interfering substances

Tests were made to see what the effect of other gases on the emission from the detector would be if they were simultaneously eluted with sulphur compounds from a column. Samples of pure hydrocarbon alone were injected into the hydrogen flame and a response was observed, though of a fairly weak nature, *e.g.* 1 ml of methane gave a similar response to 1 ml of nitrogen containing 1 p.p.m. (v/v) S as H_2S. Examination of the spectrum of the flame when hydrocarbons were added to it showed the emission was negligible in the 370–380-nm region but appreciable at 394 nm. Since there was a further S_2 band head at 376 nm of nearly the same intensity as at 394 nm, the filter was replaced by one of a broader bandwidth (Baird Atomic RD/UV, bandwidth at half-peak—15 nm) with peak transmission at 375 nm.

When mixtures of sulphur compounds and hydrocarbons were subsequently injected, it was found that the response was less than for an equivalent amount of sulphur admixed with nitrogen. Larger samples gave progressively smaller responses, leading to complete suppression of the signal. Similarly, increasing the carbon number of the diluting gas in the order ethane, propane, butane, also diminished the signal. It was thus evident that the sulphur emission was obscured by the presence of hydrocarbons in the flame and this effect swamped any emission in the spectral region concerned. When the diluent gas was carbon dioxide, interference was much less, and even for the largest samples the signal was only decreased in comparison with that for nitrogen (by about 25–30%) and complete suppression was not observed.

Incorporation of the burner in a gas chromatograph

Though the burner had been used with a chromatographic column in some of the above experiments, it was thought that its performance could be improved by the use of a higher powered photomultiplier (Mullard, type 150 UVP) and by fixing the unit permanently to a gas chromatograph. The burner assembly in an aluminium casing was thus attached to a blank head unit of a Pye Type 104 chromatograph and the column outlet attached directly to the base of the burner where the carrier gas was admixed with hydrogen. For convenience the photomultiplier and dynode were housed in a Unicam hollow-cathode lamp holder (Mk 1) which was plugged as a complete assembly into a socket in the burner enclosure. Because of the larger diameter of the photo-tube, the interference filter was also increased in size to 2″ × 2″. Hydrogen and oxygen for the detector were supplied via micrometer needle valves and the carrier gas was controlled by a mass flow controller to permit programmed temperature operation of the chromatograph if required. The complete unit is shown in Fig. 4.

Development of a burner for the determination of total sulphur in hydrocarbons

The previous experiments showed that any attempts to determine the total sulphur present in a complex hydrocarbon mixture in which several sulphur compounds

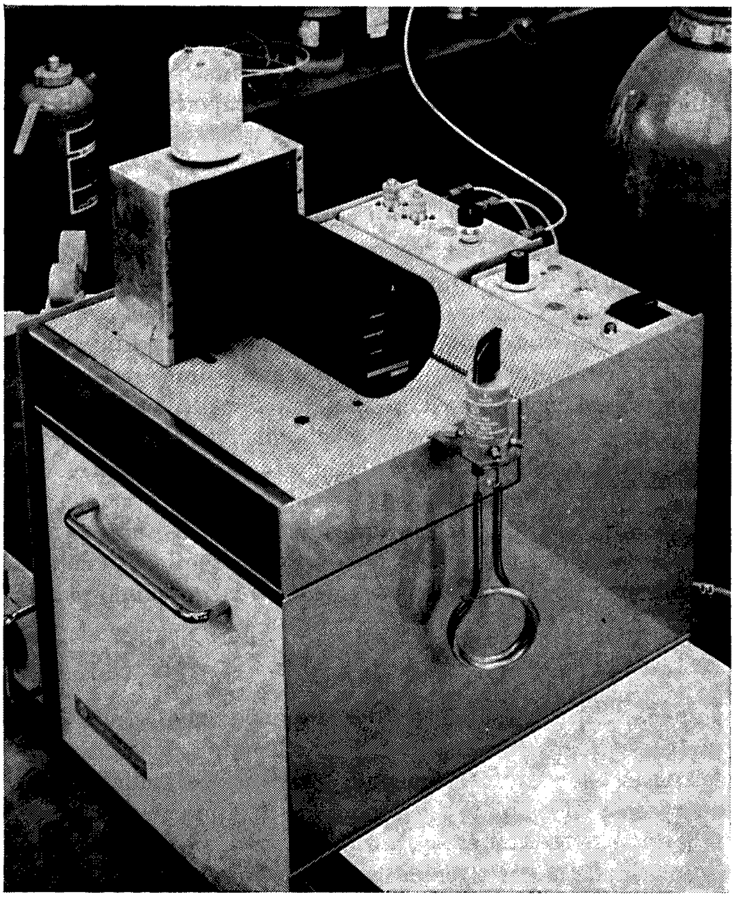

Fig. 4. Detector and phototube fitted to a gas chromatograph.

were present would result in formidable calibration difficulties if gas chromatographic methods were employed. A preferable approach therefore was the removal of the interfering hydrocarbons and the conversion of the separate sulphur compounds into one compound. Combustion was the obvious method, but there remained the choice of whether it should be done in a flow system with the oxidation products entering a detector continuously, or whether discrete samples should be taken as in a chromatograph and the sulphur oxides concentrated before admission to a detector. The latter method was first attempted, using a modified Schöniger combustion[14] apparatus which could be purged with gas after combustion. The difficulties of first trapping and then desorbing the sulphur compounds reproducibly proved to be intractable, so that the continuous process was investigated. The main difficulties then encountered were the stabilisation of a combustion flame, so that different hydrocarbon mixtures could be successfully oxidised, and secondly, loss of sulphur by adsorption on the apparatus walls before the oxidized products had reached the detector burner. The former difficulty was overcome by injecting the hydrocarbon into a hydrogen flame and the second by positioning the oxidising flame directly beneath the detecting flame. The complete unit was made in transparent silica, mounted within a light-tight box, and is shown in Fig. 5.

The combined burners required a special ignition procedure and the following sequence of operations was followed. All gas supply lines were first purged with the appropriate gas and then the supplies were shut off. The vaporizer heater was

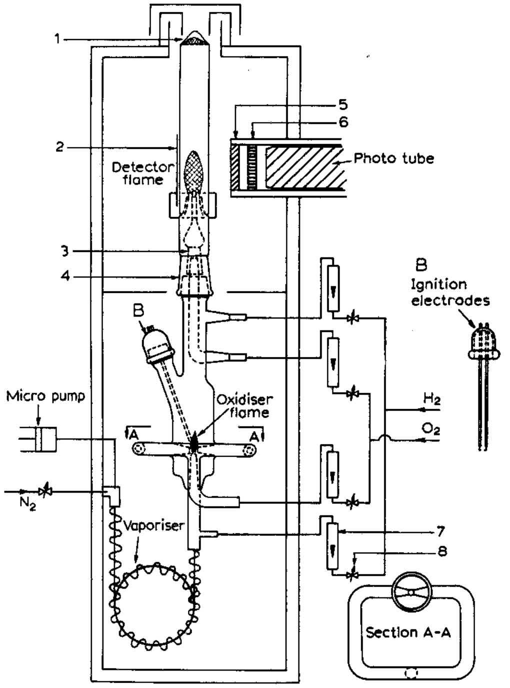

Fig. 5. Combined oxidiser and detector burner. (1) Burning excess hydrogen, (2) reflector, (3) B5 cone and socket, (4) B14 cone and socket, (5) heat filter, (6) UV filter, (7) flowmeter, (8) needle valve.

switched on and when the operating temperature (225°) had been obtained, the sample to be analysed was pumped in from a Braun Perfusor micropump and the carrier nitrogen supply started. The gas flows are given in Table II.

The hydrogen supply to the lower burner was then commenced and after the apparatus had been purged free of oxygen, a continuous HT discharge was applied across the platinum ignition electrodes. The oxygen supply was cautiously opened until a stable flame was established and then the oxygen adjusted until the yellow tip of the flame had disappeared.

TABLE II

SAMPLES AND GAS FLOWRATES FOR COMBINED OXIDISER/DETECTOR BURNER

Sample	*Flowrates*		
Petroleum distillate		H_2 (for detector)	430–485 ml/min
Distillate	0.9–1.1 ml/h (liquid)	O_2 (for detector)	25–45 ml/min
N_2	100–110 ml/min		
H_2 (for oxidiser)	40–50 ml/min		
O_2 (for oxidiser)	70–80 ml/min		
Hydrocarbon gas, incl. natural gases			
Gas	50–70 ml/min		
H_2 (for oxidiser)	50–70 ml/min		
O_2 (for oxidiser)	170–190 ml/min		

The hydrogen supply to the detector was then mixed with the combustion products and a flame lit at the top of the exhaust tube. At this stage, if excess of oxygen from the oxidation burner were present, the flame on the exhaust tube would burn erratically and a slight reduction of oxygen to the oxidiser would have to be made. Finally, oxygen was admitted through the central capillary to the detector section until a strike back of the flame occurred and a stable flame was established. When the apparatus was warm some slight adjustments sometimes had to be made to counteract changes in flame speed. By supplying hydrogen to the oxidation burner, this flame could be maintained with a wide range of distillates, the flame speed of hydrogen being sufficiently high to stabilize the flame irrespective of the flame speed of the vaporized hydrocarbons. When gas samples were being analysed, the vaporizer could be omitted, and if hydrogen was already present in the gas (*e.g.* town gas), no addition of hydrogen was necessary. Different gas flows were required depending on whether liquid or gas was being sampled (see Table II).

DISCUSSION

The sulphur photometric detector has two disadvantages as a quantitative detector for gas chromatography. Because of the non-linearity of the response, it must be calibrated for each compound separately and results should be interpolated on a calibration graph. Even so, because of inflection points on the calibration graphs there will be areas of uncertainty in any calibration. In addition, there is the possibility of interference if separation of the sulphur compounds from other hydrocarbons is not complete. This is probably a negligible effect unless a large hydrocarbon peak is being eluted simultaneously with a small sulphur peak, but this is always a possibility. Though this latter difficulty could be overcome by the use of the combined oxidiser/detector burner on a chromatograph, some sensitivity would be lost since this unit is undeniably less sensitive than the simple burner because of the dilution of the sample with considerable quantities of combustion products. For qualitative chromatographic analysis therefore, or when interfering hydrocarbons are insignificant, and few sulphur compounds are present, the simple burner is to be preferred.

However, the chromatography of sulphur compounds poses other problems. The reactivity of these compounds is such that they react with the materials of the apparatus and the column support, and, as in many other chromatographic analyses, conditioning of the apparatus with several repeated samples, or with "conditioning" samples of a high sulphur content, is necessary before reliable quantitative analyses can be achieved.

Silanisation of the column and support and the use of aluminium tubes lessen the effect, but even then the quantity eluted may only be a fraction of the initial sample. Maman[15] has reported that when a mass-sensitive microcoulometric detector responding to sulphur is used, only 70% of a heterocyclic sulphur compound and only 10–40% of a mercaptan could be recovered from a column packed with SE 30 silicone rubber. For this reason the use of the continuous sulphur detector offers advantages, as the sample lines and apparatus are continuously subjected to the presence of the sulphur compounds, and while there may be some delay in recording a change in concentration, it would probably be less than in any chromatographic system. Though there is interference of the output arising from carbon dioxide produced by the oxidiser flame, this is constant for a given feed.

Applications

The gas chromatograph unit has mainly been used for the qualitative detection of sulphur in hydrocarbon samples. Typical of this use is the chromatogram (Fig. 6) of traces of sulphur compounds present in the products from an experiment to hydrogenate distillate. A 20% squalane on Embacel column was used with argon as carrier gas and temperature programming as indicated.

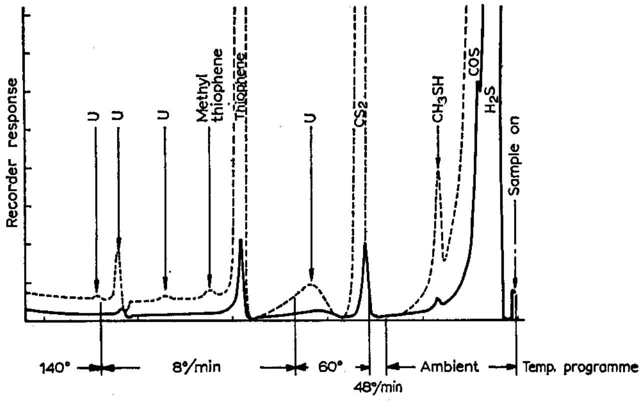

Fig. 6. Sulphur compounds in gas from hydrogenator. (U) unknown compounds. (——) 200 mV for f.s.d. (-----) 50 mV for f.s.d. H_2S *ca.* 1900 p.p.m. Total S *ca.* 2000 p.p.m.

The concentration of sulphur dioxide in the combustion products of gas burners could be determined at as low a level as 0.04 p.p.m. in a 10-ml sample of gas with the same column. Odorants in process gas and natural gas (tetrahydrothiophene or dimethyl sulphide) were detectable at 0.05 p.p.m. (v/v) with a temperature-programmed SE-30 column.

The total sulphur burner was calibrated for liquid samples with solutions of thiophene in previously desulphurized light distillate (FBP 170°) giving a concentration range of 20–300 p.p.m. S (w/w) (Fig. 7). At lower levels than 20 p.p.m., the signal-to-noise ratio was excessive; it arose from fluctuations in the rate of delivery of the hydrocarbon from the micropump, since with gases this difficulty was not experienced and lower levels could be detected.

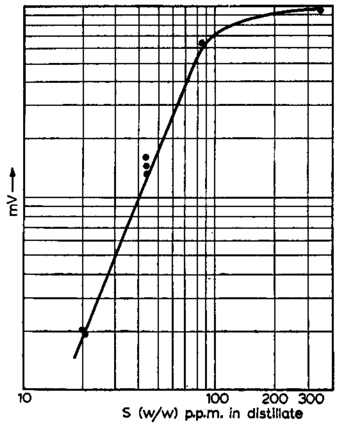

Fig. 7. Calibration graph for thiophene in distillate.

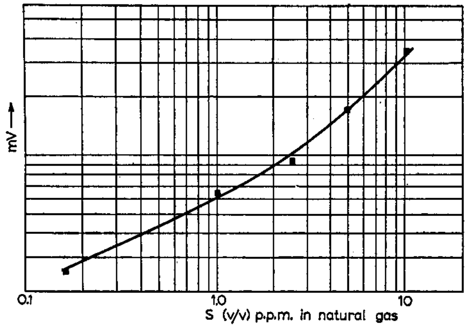

Fig. 8. Calibration graph for hydrogen sulphide in natural gas.

For gases the instrument was calibrated by the addition of hydrogen sulphide to hydrocarbon gases, the mixtures prepared being in the range 0.1–10 p.p.m. S (v/v) (1 p.p.m. S (v/v) is *ca.* 2 p.p.m. S (w/w)) (Fig. 8). The sulphur content was checked independently by the methylene blue method. The burner has been successfully used in the on-stream monitoring of hydrocarbon gases to determine the odorant content of the gas in a range 0.1–10 p.p.m. (v/v).

CONCLUSIONS

The flame emission detector is a useful addition to the growing number of selective detectors used in gas chromatography. It does, however, require considerable care for quantitative use and it must be appreciated that calibration is often difficult and can be unsatisfactory over some ranges of concentration. It is, however, of use in the 0.1–100 p.p.m. range if suitable calibrations are made. For the continuous measurement of total sulphur, the combined oxygen burner and detector is more suitable and levels of 20–100 p.p.m. (w/w) in liquids and 0.2–10 p.p.m. (v/v) in gases have been successfully measured. By this method of measurement, many of the difficulties inherent in chromatographic determinations of sulphur compounds are avoided.

The authors would like to thank Mr. V. J. MORRIS for his practical help in building the apparatus, Mr. T. A. DICK of the West Midlands Gas Board for the facilities provided for the field trials and the Gas Council for permission to publish this paper. The advice of Mr. S. BRODY, Melpar Inc., is gratefully acknowledged. The quartz burners were made by Midland Scientific Glassblowing, Cherry Orchard, Lichfield.

SUMMARY

Hydrogen-rich flames are rapidly assuming an important role as highly sensitive detectors for sulphur. S_2-species are generated in the flame and the radiation emitted by them is measured in the UV range. A preliminary separation of sulphur, *e.g.* by chromatography, is required for analysis of samples in which sulphur is associated with hydrocarbons, as in gas, fuel and petroleum samples, since hydrocarbons cause the emission to be diminished in proportion to both the concentration and number of carbon atoms per molecule of hydrocarbon. The quenching effect on the emission by carbon present as dioxide is negligible when compared with its effect when present as hydrocarbon. This finding has led to the use of preliminary oxidation to avoid the need of prior separation. A complete apparatus, which includes a stacked burner system, is described. Continuous monitoring of sulphur in a stream of hydrocarbon gases is possible.

RÉSUMÉ

Les flammes riches en hydrogène constituent des détecteurs très sensibles pour le soufre. Des molecules S_2 formées dans la flamme émettent une radiation dans l'ultraviolet, qui peut être mesurée. Une séparation préliminaire du soufre, par exemple par chromatographie, est nécessaire pour l'analyse d'échantillons dans lesquels le soufre est associé à des hydrocarbures (gaz, fuel, pétrole), puisque l'émission est reduite par les hydrocarbures. Cette reduction d'émission est proportionnelle à la concentration et au nombre des atomes dans chaque molecule de l'hydrocarbure. L'influence du carbone dans l'anhydride carbonique sur l'émission est négligeable, en comparaison avec son influence en forme d'hydrocarbure. On peut procéder à une oxydation préliminaire pour éviter une séparation préalable. On décrit un appareillage complet à bruleur double. Un contrôle continu du soufre dans un courant d'hydrocarbures gazeux est possible.

ZUSAMMENFASSUNG

Wasserstoffreiche Flammen werden in immer stärkeren Masse als hochempfindliche Detektoren für Schwefel verwendet. Dabei werden in der Flamme S_2-Spezies gebildet und die emittierte Strahlung im UV gemessen. Eine vorhergehende chromatographische Abtrennung des Schwefels ist in solchen Proben erforderlich, in denen Schwefel von Kohlenwasserstoffen begleitet wird wie z.B. in Gasen, Brenn-

stoffen und Heizölen, da durch die Kohlenwasserstoffe die Emission verringert wird, und zwar proportional sowohl zu ihrer Konzentration als auch zur Zahl der Kohlenstoffatome pro Molekül. Der Quensch-Effekt auf die Emission durch Kohlenstoffdioxyd ist vernachlässigbar, wenn er mit dem Effekt in Gegenwart von Kohlenwasserstoff verglichen wird. Dieses Ergebnis führte zu vorhergehender Oxydation, um eine Trennung zu vermeiden. Eine Apparatur, die es ermöglicht den Schwefel kontinuierlich in Kohlenwasserstoffgasen zu bestimmen wird beschrieben.

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A SPECTROPHOTOMETRIC STUDY OF THE IRON(III)–PHENOL REACTION

GLENN LIMB AND REX J. ROBINSON
Chemistry Department, University of Washington, Seattle, Wash. 98105 (U.S.A.)

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The color reaction between iron(III) chloride and phenols has been used for many years as a standard method for the detection of phenolic compounds. Many investigators have employed spectrophotometric methods to study this reaction but with conflicting results. BROUMAND AND SMITH[1] using JOB's method of continuous variation[2], concluded that iron(III) combines with many substituted phenols in a 1:1 ratio. However, they indicated that their results with iron(III) and phenol were inconclusive. MILBURN[3], and ERNST AND HERRING[4] have determined equilibrium constants for the formation of the 1:1 iron(III)–phenol complex. GORE AND NEWMAN[5] and others[6,7] have recorded the existence of the 1:3 iron(III)–phenol complex. Still other iron(III)–phenol complexes have been suggested by other authors[8,9]. The exact nature of the reaction does not appear to be thoroughly understood as yet.

In the present spectrophotometric study, the continuous variation method was applied to iron(III) nitrate–phenol solutions at pH 1.0; the results indicated a 1:1 complex that was but slightly associated. Continuous variation curves at higher pH values and without pH control produced inconclusive results which can be explained by considering the reduction in the iron(III) ion concentration through hydrolysis and by changes in the hydrogen ion concentration. Additional spectrophotometric studies have been made to estimate the equilibrium constant of the iron(III)–phenol reaction and to investigate the constancy of the colored complex.

The application of the continuous variation method to a slightly associated 1:1 complex does not appear to have been described in the literature, although the method is accepted as appropriate for complexes that are in equilibrium with dissociated species. The following discussion is presented to establish the relationship of the absorbance of continuous variation solutions to the formal concentration of the reactants which are but slightly associated.

Under ideal conditions when a metal ion (M) and a ligand (L) exist in equilibrium with a 1:1 metal–ligand complex (ML) as

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad \text{(ionic charges omitted)}$$

the concentration of the metal–ligand complex [ML] can be expressed in terms of the metal ion concentration [M] and free ligand concentration [L] and the equilibrium constant (K_e) by the equations

$$[\mathrm{ML}] = K_e[\mathrm{M}][\mathrm{L}] \tag{1a}$$

$$= K_e([\mathrm{M}]_0 - [\mathrm{ML}])([\mathrm{L}]_0 - [\mathrm{ML}]) \tag{1b}$$

$$\cong K_e[\mathrm{M}]_0[\mathrm{L}]_0 \tag{1c}$$

where $[M]_0$ and $[L]_0$ represent the initial formal concentration of metal ion and ligand respectively. The expression (1c) is a simplified approximation of (1b) that is applicable to a slightly associated complex when the complex is formed to the extent of 1% or less, *i.e.* $[ML] \ll [M]_0$ and $[L]_0$.

If the complex absorbs radiation at some wavelength where neither the free metal ion nor free ligand interferes and the absorbance (A) of the complex follows Beer's law then

$$A = k[ML] \tag{2a}$$

$$\cong kK_e[M]_0[L]_0 \cong K_1[M]_0[L]_0 \tag{2b}$$

Thus both the complex concentration [ML] and the absorbance (A) would be directly proportional to the metal ion–ligand formality product, $[M]_0[L]_0$.

In the continuous variation method the sum of the metal ion and ligand formalities in each solution of a given series is kept constant at some optimum value, C_x

$$[M]_0 + [L]_0 = C_x \tag{3}$$

The ratio of metal ion to ligand formality in the various solutions is varied as desired and the absorbance readings taken of each solution. In Table I the absorbance values of a continuous variation application to solutions containing a slightly associated metal–ligand complex have been determined using eqn. (2b). The absolute absorbance (A) has no defined value; however the relative absorbances (A/A_r) of the various solutions, using the absorbance of the solution containing metal and ligand in a 1:1 ratio as a reference absorbance (A_r), have definite characteristic values. Two continuous variation curves (lines) having these characteristic relative absorbance values are shown in Fig. 1.

TABLE I

ABSORBANCE VALUES OF A CONTINUOUS VARIATION SERIES INVOLVING THE FORMATION OF A SLIGHTLY ASSOCIATED 1:1 METAL–LIGAND COMPLEX

Metal-ion formality $[M]_0$	*Ligand formality* $[L]_0$	*Absolute absorbance* A	*Relative absorbance* A/A_r
0.0	C_x	0.00	0.000
$0.1C_x$	$0.9C_x$	$0.09C_x^2K_1$	0.360
$0.2C_x$	$0.8C_x$	$0.16C_x^2K_1$	0.640
$0.3C_x$	$0.7C_x$	$0.21C_x^2K_1$	0.840
$0.4C_x$	$0.6C_x$	$0.24C_x^2K_1$	0.960
$0.5C_x$	$0.5C_x$	$0.25C_x^2K_1(A_r)$	1.000
$0.6C_x$	$0.4C_x$	$0.24C_x^2K_1$	0.960
$0.7C_x$	$0.3C_x$	$0.21C_x^2K_1$	0.840
$0.8C_x$	$0.2C_x$	$0.16C_x^2K_1$	0.640
$0.9C_x$	$0.1C_x$	$0.09C_x^2K_1$	0.360
C_x	0.0	0.00	0.000

If the formation of the metal–ligand complex involves the release of hydrogen ions, as

$$M + LH \rightleftharpoons ML + H^+$$

the complex concentration can be expressed by the following equations:

$$[ML] = \frac{K_e[M][LH]}{[H^+]} \cong \frac{K_e[M]_0[LH]_0}{[H^+]} \qquad (4)$$

when $[ML] \ll [M]_0$ and $[L]_0$. The absorbance, providing Beer's law is valid, can be expressed as

$$A = k[ML] \cong \frac{kK_e[M]_0[LH]_0}{[H^+]} \cong \frac{K_1[M]_0[LH]_0}{[H^+]} \qquad (5)$$

The metal–ligand solutions would have absorbance values that are directly proportional to their respective metal ion–ligand formality products and inversely proportional to their respective hydrogen ion concentrations. If a valid plot by the continuous variation method is desired for this type of equilibrium, the hydrogen ion concentration of all solutions must be maintained constant at some suitable value. The absorbance values for these solutions could then be expressed as

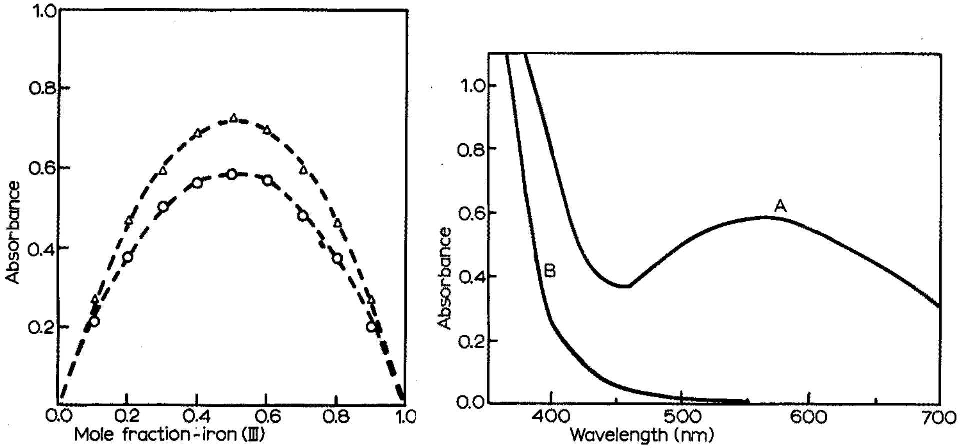


Fig. 1. Continuous variation curves of iron(III) nitrate–phenol solutions at pH 1.0. (○) $C_1 = [Fe^{3+}]_0 + [\varphi OH]_0 = 0.150\ F$; (△) $C_2 = [Fe^{3+}]_0 + [\varphi OH]_0 = 0.167\ F$. Dashed lines indicate ideal absorbance curves characteristic of a slightly associated 1:1 complex (Table I).

Fig. 2. Absorbance spectrum of an iron(III) chloride–phenol aqueous solution. (A) 0.06 *F* phenol, 0.0033 *F* iron(III) chloride; (B) 0.0033 *F* iron(III) chloride.

$$A \cong K_2[M]_0[LH]_0 \qquad (6)$$

When the hydrogen ion concentration of the solutions used in the continuous variation method is controlled at some definite value, the resulting relative absorbance values would be identical to those given in Table I.

EXPERIMENTAL

The reaction of iron(III) nitrate with phenol was investigated by the continuous variation method at controlled pH values of 1.0, 1.4, 2.0 and without pH control.

Reagent preparation

All reagent solutions of iron(III) nitrate and phenol were adjusted to the desired pH in the following manner. The required amount of phenol or iron(III) nitrate was dissolved in *ca.* 4/5 the volume of water necessary to give the desired formality. The pH was then adjusted to the desired value by adding nitric acid or sodium hydroxide using a Beckman Zeromatic glass electrode pH meter. The solution was then diluted to the required volume with a diluent solution (distilled water that had been adjusted to the desired pH with nitric acid).

The following solutions were prepared for conducting the continuous variation studies: (*a*) at pH 1.0, 0.3 F iron(III) nitrate and 0.3 F phenol, (*b*) at pH 1.4, 0.2 F iron(III) nitrate and 0.2 F phenol, (*c*) at pH 2.0, 0.08 F iron(III) nitrate and 0.08 F phenol (the solution of 0.08 F iron(III) nitrate, prepared by adding sodium hydroxide to obtain a pH of 2.0, was initially cloudy but became clear after standing for 3–4 h), (*d*) for uncontrolled pH, 0.1 F iron(III) nitrate and 0.1 F phenol.

General continuous variation procedure

The reagent solutions of iron(III) nitrate and phenol were blended in accordance with the scheme presented in Table II. The given volume of diluent was added for adjustment of the iron(III) ion and phenol concentrations to give a proper absorbance range of the mixed solutions. No detectable changes in pH were observed with the mixing of the various reagent solutions. The absorbance readings were taken in 1-cm cuvettes with a Bausch and Lomb Spectronic 20 at 600 nm immediately after mixing the reagent solutions. The absorbance measurements were made at 600 nm rather than at 560 nm, the wavelength of maximum absorbance (Fig. 2), because of less interference from iron(III) ion. The interference at 600 nm was relatively insignificant for the iron(III) nitrate solutions used at pH values of 1.0 and 1.4, but was considerable at pH 2.0. It was therefore necessary to correct the absorbance values of iron(III) nitrate–phenol solutions used at pH 2.0 by subtracting the absorbance of a solution containing an equivalent iron(III) nitrate concentration.

TABLE II

CONTINUOUS VARIATION DATA OF IRON(III) NITRATE–PHENOL SOLUTIONS, pH 1.0

Reagents added (ml) (plus 10 ml diluent)		*Formality*		*Absorbance*	
φOH 0.3 F	Fe^{3+} 0.3 F	$[\varphi OH]_0$	$[Fe^{3+}]_0$	A	A/A_r
		C_1			
9	1	0.135	0.015	0.210	0.364
8	2	0.120	0.030	0.375	0.647
7	3	0.105	0.045	0.485	0.835
6	4	0.090	0.060	0.560	0.965
5	5	0.075	0.075	0.580(A_r)	1.000
4	6	0.060	0.090	0.565	0.970
3	7	0.045	0.105	0.480	0.830
2	8	0.030	0.120	0.370	0.640
1	9	0.015	0.135	0.200	0.348

RESULTS AND DISCUSSION

The continuous variation absorbance curves of iron(III) nitrate-phenol solutions at pH 1.0 (Fig. 1, Table II) are in close agreement with those characteristic of a slightly associated 1:1 complex (Fig. 1, Table I). A slight association of iron(III) with phenol forming a 1:1 colored complex would require that the absorbances of the mixtures be dependent upon the iron(III)-phenol formality product, $[Fe^{3+}]_0[\varphi OH]_0$ (eqn. (2)). This relationship should exist if there are no interfering equilibrium reactions and if Beer's law is applicable to the absorbance of the colored complex. A comparison of absorbances of solutions with those twice as concentrated in phenol and one-half as concentrated in iron(III) nitrate (Table III) indicates that solutions possessing equivalent iron(III)-phenol formality products have nearly equivalent absorbances although the relative concentrations of iron(III) and phenol may vary considerably. This relationship is adequately explained if iron(III) and phenol are only slightly associated as a 1:1 colored complex. Otherwise the results are difficult to interpret.

TABLE III

COMPARISON OF ABSORBANCES OF IRON(III)-PHENOL SOLUTIONS OF VARIOUS CONCENTRATIONS, pH 1.0

Formality		*Formality product* $[\varphi OH]_0[Fe^{3+}]_0 \cdot 10^3$	*Absorbance*
$[\varphi OH]_0$	$[Fe^{3+}]_0$		
0.150	0.017	2.56	0.265
0.300	0.0085	2.56	0.265
0.133	0.034	4.53	0.465
0.266	0.017	4.53	0.460
0.117	0.050	5.85	0.590
0.234	0.025	5.85	0.590
0.100	0.067	6.70	0.685
0.200	0.034	6.70	0.685
0.083	0.083	6.90	0.720
0.166	0.042	6.90	0.720
0.067	0.100	6.70	0.695
0.134	0.050	6.70	0.675
0.050	0.117	5.85	0.590
0.100	0.059	5.85	0.580
0.034	0.133	4.53	0.460
0.068	0.067	4.53	0.450
0.017	0.150	2.56	0.265
0.034	0.075	2.56	0.250

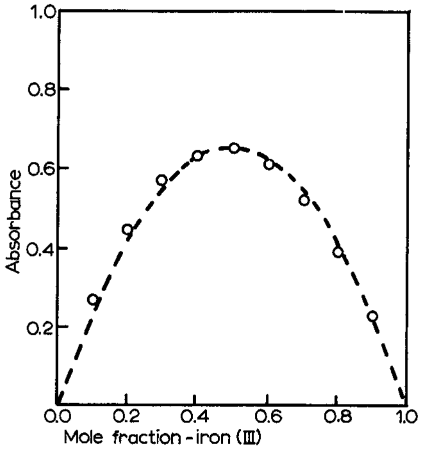
The continuous variation curves of iron(III) nitrate-phenol solutions at pH 1.4 and 2.0 vary from the curve characteristic of a slightly associated 1:1 complex (Figs. 3 and 4). This disagreement can be largely explained by the hydrolytic reaction of iron(III) forming a dimeric ionic species[10].

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$$

The equilibrium expression for this reaction is

$$\frac{[Fe_2(OH)_2^{4+}][H^+]^2}{[Fe^{3+}]^2} = 1.2 \cdot 10^{-3} \tag{7}$$

Equation (7) has been employed to estimate the relative quantities of iron(III) monomer and dimer existing in iron(III) nitrate solutions of varying concentration and pH. In Fig. 5 the approximate fraction of iron(III) existing in the monomeric form is plotted against the total formal concentration of iron(III) for iron(III) nitrate solutions of pH 1.0, 1.4 and 2.0. The degree of dimerization is large for solutions at pH 2.0, moderate for solutions of pH 1.4 and relatively small for solutions of pH 1.0.



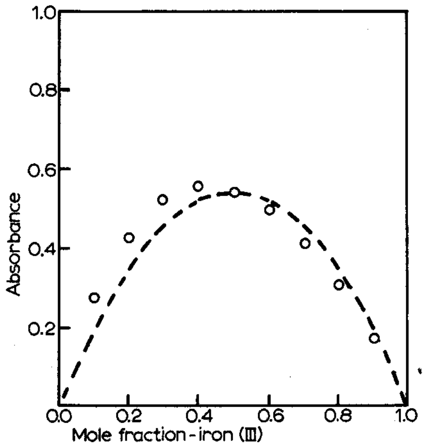
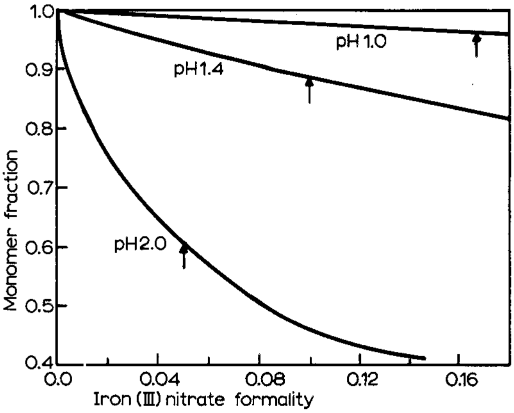


Fig. 3. Continuous variation curve of iron(III) nitrate–phenol solutions at pH 1.4. (○) $[Fe^{3+}]_0 + [\varphi OH]_0 = 0.10$ *F*. Dashed line indicates ideal absorbance curve characteristic of a slightly associated 1:1 complex.

Fig. 4. Continuous variation curve of iron(III) nitrate–phenol solutions at pH 2.0. (○) $[Fe^{3+}]_0 + [\varphi OH]_0 = 0.053$ *F*. Dashed line indicates ideal absorbance curve characteristic of a slightly associated 1:1 complex.



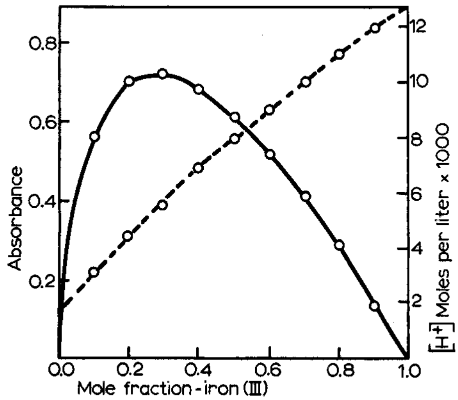
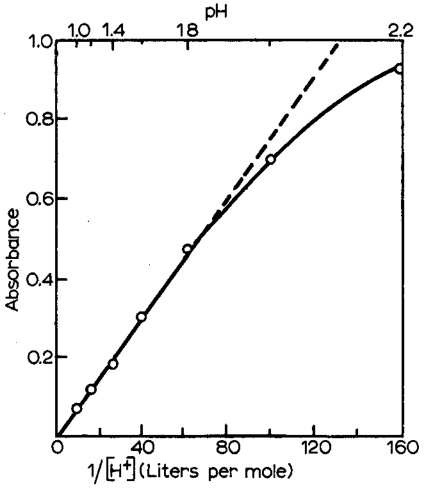


Fig. 5. Fraction of free monomeric iron(III) *vs.* total iron(III) concentrations for iron(III) nitrate. Solutions of pH 1.0, 1.4, and 2.0. Arrows indicate the highest iron(III) formality of solutions used in continuous variation method at the respective pH.

Fig. 6. Continuous variation curve of iron(III) nitrate–phenol solutions without pH control. (———) Absorbance curve; (------) hydrogen ion concentration curve. $[Fe^{3+}]_0 + [\varphi OH]_0 = 0.05$ *F*.

The dimerization effect is deemed sufficient to alter the association equilibrium of monomeric iron(III) with phenol in iron(III) nitrate–phenol solutions of pH 1.4 and 2.0. Any continuous variation curve of iron(III) nitrate–phenol solutions at these pH values should not be expected to give true representation of the composition of the complex.

A continuous variation absorbance curve of iron(III) nitrate–phenol (without pH control) and the hydrogen ion concentration of the respective solutions have been plotted concurrently in Fig. 6. The absorbance curve is indicative of the formation of a complex containing 3 phenols to 1 iron(III) ion. However, the effect of increasing acidity of these solutions with increasing iron(III) nitrate concentration must be considered. The absorbance of solutions constant in their concentrations of iron(III) nitrate and phenol but containing varying quantities of nitric acid exhibited a near inverse relationship to the hydrogen ion concentration within a pH range of 1.0 to 2.0 (Fig. 7). This clearly demonstrates the necessity for pH control in the continuous variation experiments. It was for this reason that the pH was maintained at pH 1 for the continuous variation studies recorded in Fig. 1 and Table II where a 1:1 ratio was indicated for the iron(III)–phenol complex.



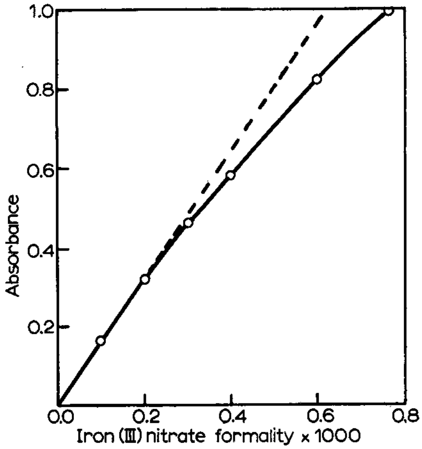


Fig. 7. The effect of hydrogen ion concentration upon complex formation. All solutions 0.008 *F* in iron(III) nitrate and 0.08 *F* in phenol. Dashed line is extension of lower linear segment.

Fig. 8. Absorbance values for iron(III) nitrate solutions with a large excess of phenol (0.766 *F*).

Equilibrium constant determination

The previous spectrophotometric studies have indicated the formation of a slightly associated 1:1 iron(III)–phenol complex with the release of hydrogen ions as represented by the equation

$$Fe^{3+} + \varphi OH = FeO\varphi^{2+} + H^+$$

The equilibrium constant expression is

$$\frac{[FeO\varphi^{2+}][H^+]}{[Fe^{3+}][\varphi OH]} = K_e \tag{8a}$$

For slightly associated complexes this equilibrium would be represented by eqn. (8b)

$$\frac{[\mathrm{FeO}\varphi^{2+}][\mathrm{H}^+]}{[\mathrm{Fe}^{3+}]_0[\varphi\mathrm{OH}]_0} \cong K_e \tag{8b}$$

The continuous variation data of Table II give values for $[\mathrm{Fe}^{3+}]_0$, $[\varphi\mathrm{OH}]_0$ and $[\mathrm{H}^+]$ for several solutions. The concentration values for the iron(III)–phenol complex, $[\mathrm{FeO}\varphi^{2+}]$, in the various solutions also must be known before the equilibrium constant can be calculated. The concentration of the complex was related to absorbance in solutions where the iron(III) ion was assumed to be completely converted to complex by the mass action effect of a large excess of phenol (a nearly saturated solution) as shown in Fig. 8. The linear segment (extended) of Fig. 8 was used to convert solution absorbance to the concentration of ferric–phenol complex in some continuous variation solutions of Table I. The equilibrium constant was estimated from the data given for these solutions, and is listed in Table IV. The approximate percentage of iron(III) ion that was complexed in each of the solutions also was calculated and is included in Table IV.

TABLE IV

DETERMINATION OF THE EQUILIBRIUM CONSTANT AND THE PERCENTAGE OF COMPLEX FORMATION OF VARIOUS IRON(III)–PHENOL SOLUTIONS (23.2°)

Formality		*Absorbance*	*Complex concn. (moles/l) · 10⁴*	*Equilibrium constant · 10³*	*% Fe^{3+} complexed*
$[\varphi OH]_0$	*$[Fe^{3+}]_0$*				
pH 1.0					
0.135	0.015	0.210	1.4	6.7	0.9
0.105	0.045	0.485	3.2	6.7	0.7
0.075	0.075	0.580	3.8	6.7	0.5
0.150	0.017	0.265	1.7	6.7	1.0
0.117	0.050	0.590	3.9	6.6	0.8
0.083	0.083	0.720	4.7	6.8	0.6
pH1.4					
0.090	0.010	0.270	1.8		1.8
0.050	0.050	0.654	4.2		0.9
pH 2.0					
0.047	0.005	0.275	1.8		3.4
0.027	0.027	0.540	3.5		1.3

The estimated value of the equilibrium constant ($6.7 \cdot 10^{-3}$) obtained by us agrees quite well with the value of $1.5 \cdot 10^{-2}$ of MILBURN[3] and the value of $1.7 \cdot 10^{-2}$ of ERNST AND HERRING[4]. Both of these values were recalculated by us for hydrogen ion effect to make them comparable; the two values are calculated values obtained by multiplying the reported values[3,4] by the ionization constant of phenol to incorporate the effect of hydrogen ion concentration into the equilibrium and make all the values comparable. The accuracy of the proposed value is dependent on the validity of the assumption that the iron(III) ion of the solutions of Fig. 8 is almost totally converted to the complex by the large excess of phenol. If a significant amount of iron(III) were left unconverted, then the calculated value of the equilibrium constant would be larger than the true value.

The small value of the equilibrium constant illustrates the weak association of iron(III) with phenol at low pH values and any competition from other iron(III) complexing ligands including chloride would significantly alter the degree of association of iron(III) and phenol. The association of iron(III) with phenol appears to be relatively independent of ionic strength as sodium nitrate concentrations of up to 1.0 *F* did not appreciably affect the absorbance of an iron(III)–phenol solution.

Variation of absorbance of some iron(III) nitrate–phenol mixtures with time

A relatively rapid decrease in absorbance with time occurred in mixtures containing a high concentration of phenol and a low concentration of iron(III) (Fig. 9, curve B). The apparent cause of the fading was the partial reduction of iron(III) to iron(II) by the phenol. The formation of iron(II) in these solutions was verified by testing with a 1% *o*-phenanthroline solution. When iron(II) was initially present in high phenol–low iron(III) mixtures, the extent and rate of fading was significantly decreased (Fig. 9, curve A). This indicates a reverse mass action effect which retards the reduction of the iron(III).

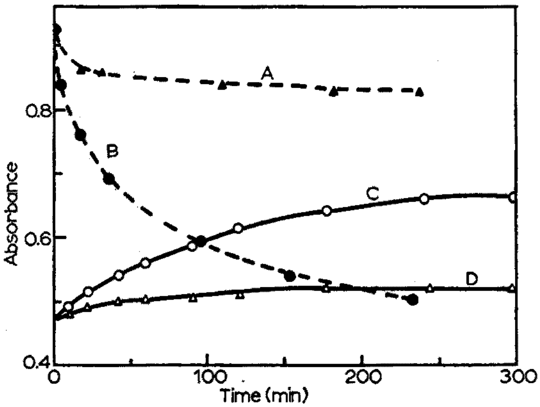


Fig. 9. Absorbance *vs.* time curves of various iron(III) nitrate–phenol solutions.

(A)	0.64 *F*	φOH	0.0008 *F*	$Fe(NO_3)_3$	0.02 *F*	$FeCl_2$
(B)	0.64 *F*	φOH	0.0008 *F*	$Fe(NO_3)_3$		
(C)	0.025 *F*	φOH	0.025 *F*	$Fe(NO_3)_3$	0.10 *F*	$Ba(NO_3)_2$
(D)	0.025 *F*	φOH	0.025 *F*	$Fe(NO_3)_3$	0.10 *F*	$Fe(NO_3)_2$

Mixtures nearly equivalent in iron(III) and phenol concentrations showed a moderate increase in absorbance with time (Fig. 9, curve C). The absorbance increase was significantly less when the complex was formed in the presence of the iron(II) (Fig. 9, curve D). It is suggested that the increase in absorbance of these solutions may be due to the reaction of iron(III) with an oxidation product of phenol to form a highly colored complex. Catechol (1,2-dihydroxybenzene) is a possible oxidation product and is known to react with iron(III) to form a strongly associated and highly absorbing complex. No experimental evidence, however, was obtained to support this hypothesis.

SUMMARY

Iron(III) reacts with phenol to form a weakly associated complex in the ratio of 1:1. The weak association of iron(III) with phenol necessitates a correction for significant interference by dimerization of iron(III) due to hydrolysis, particularly at pH 1.4 and 2.0. It seems probable that a slower secondary reaction between iron(III) and phenol proceeds with the formation of iron(II) and a phenolic oxidation.

RÉSUMÉ

Le fer(III) réagit avec le phénol pour former un complexe faiblement associé, dans le rapport 1:1. Cette faible association nécessite une correction pour interférence par dimèrisation du fer(III) due à l'hydrolyse, particulièrement à pH 1.4 et 2.0. Il semble probable qu'une réaction secondaire plus lente entre fer(III) et phénol conduise à la formation de fer(III) et à une oxydation phénolique.

ZUSAMMENFASSUNG

Eisen(III) bildet mit Phenol einen schwach assoziierten Komplex im Verhältnis 1:1. Dadurch ist eine Korrektur für Störungen durch Dimerisation des Eisen(III) während der Hydrolyse besonders beim pH 1.4 und 2.0 erforderlich. Es scheint möglich, dass eine geringe sekundäre Reaktion zwischen Eisen(III) und Phenol die Bildung von Eisen(II) und eine Phenoloxydation fördert.

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THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN ILMENITE

E. S. PILKINGTON AND W. WILSON
Division of Mineral Chemistry, C.S.I.R.O., Port Melbourne, Victoria 3207 (Australia)

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The phosphotungstate procedure for spectrophotometric determination of vanadium suffers interference from iron, titanium and chromium[1-3] so that its application to materials such as ilmenite with V_2O_5 content in the range of 0.05–0.2% normally requires prior removal of iron and titanium by techniques such as alkaline fusion and leaching. Separations of this type, involving filtration of an oxide residue in an alkaline system, are inconvenient and may not always be quantitative. Further operations to prevent chromium interference may also be involved.

One possibility to avoid separations is to form a yellow-coloured vanadium species by evaporating an acidic solution of the sample with sulphuric acid to the fuming point in the presence of oxidising agents such as nitric acid[4] or potassium chlorate[5,6]. As this approach is free from titanium interference, preliminary tests were made with nitric acid and potassium chlorate in known systems simulating the ilmenite matrix. Consistent results could not be obtained in these tests, partly because of the ease of reduction of vanadium(V) in hot concentrated sulphuric acid. As the sensitivity was not high and control of iron interference could have been inconvenient, the technique was abandoned.

Of the organic reagents available for vanadium, hydroxamic acid derivatives give the best sensitivity and selectivity. Of these, the cupferron analogue, N-phenylbenzohydroxamic acid (N-benzoyl-N-phenylhydroxylamine) has been the most popular. Interferences from iron, titanium and chromium can still occur but can be readily overcome by masking and solvent-extraction techniques. Such techniques dispense with mercury cathode removal of iron, at one time regarded as inevitable in most procedures for low-level vanadium determinations[7].

Preliminary studies

In the first use of N-benzoyl-N-phenylhydroxylamine (BPHA) for vanadium spectrophotometry, serious interferences were observed with iron and titanium at the pH of 2–3 chosen for the reaction[8]. In a subsequent application involving materials of high titanium content, phosphoric acid and sodium fluoride were used to complex iron and titanium respectively and the BPHA–vanadium(V) compound was extracted into chloroform from either a buffered acetate system or 1 N hydrochloric acid[9]. By increasing the extraction acidity to 5–9 M in hydrochloric acid[10], interferences from iron and various other metals were eliminated without using complexing agents although the increase in acid concentration did not in fact entirely remove interference from titanium. The general suppression of interferences by operating at high acid concentrations was also reported in other work[11,12] although it was further observed that the hydrochloric acid concentration should not be higher than 4.3 *M*. Reduction of VO_2^+ to VO^{2+} by chloride ion occurs to an increasing extent with increase in hydrochloric acid concentration and only vanadium(V) gives the required reaction with BPHA. Several other workers have also indicated that reduction losses of vanadium can occur in hydrochloric acid systems at above 5 *M* concentration[13-17].

Nevertheless, hydrochloric acid systems have been preferred in almost all methods involving BPHA, because the violet-coloured reaction product formed in this medium has a higher molar absorptivity, at a peak of 535 nm, than the absorptivity obtained at a peak of 450 nm for the yellow-brown product formed in sulphuric acid systems[10]. Although a sulphuric acid system is usually involved in the decomposition of ilmenite and is a preferred medium for an oxidation of vanadium with potassium permanganate, the subsequent addition of chloride ion or hydrochloric acid can produce the purple form of the BPHA complex as effectively as in hydrochloric acid alone[10].

A study of the sulphate–chloride–BPHA system as a basis for vanadium determinations in ilmenite revealed some possible sources of error. It was confirmed that hydrochloric acid concentrations above 6 *M* cause some reduction loss of vanadium(V). Error from this source is further increased at high ambient temperatures when reinforced by the temperature rise from addition of concentrated acid to an aqueous sample solution. It was also noted that BPHA–chloroform extracts obtained directly from aqueous systems of the required acidity tended to be cloudy. Efforts to obtain clarity simply by drying were unsuccessful. The major problem was, however, the interference from titanium, a difficulty which is encountered with most vanadium reagents. Titanium forms a yellow-coloured complex with BPHA but the interference can take the form of high or low results depending on the BPHA: titanium ratio. The present experiments gave high results, in agreement with one report[17] but contrasting with low results in other work[10,12] where a smaller excess of BPHA had been used. In some procedures, particularly for low titanium levels, the interference has been ignored but as a rule fluoride complexing is adopted. This approach was considered unsatisfactory in the strongly acidic medium because of glassware attack leading rapidly to leakage from separating funnel taps.

Other methods to avoid these various sources of error were therefore investigated. It has been previously observed that the yellow BPHA–vanadium complex extracted from a sulphate medium can be converted to the purple form by scrubbing the separated extract with strong hydrochloric acid[10]. This technique was adopted in the new procedure because formation of an extracted complex in sulphate medium before contact with highly acid chloride medium eliminates risk of reduction of vanadium(V). It was seen also that the extracted vanadium complex could be quantitatively converted to the chloride form while still in contact with the original aqueous phase, thus simplifying the extraction procedure.

Efforts to prevent titanium interference at Ti:V ratios of 250:1 by adding complexing agents directly to the original extraction mixture were unsuccessful owing to the relatively high stability of the titanium–BPHA complex. As the high extraction acidity was of partial value in limiting co-extraction of titanium, the complexing agents were examined as a scrub treatment of the solvent phase. This approach formed the basis for development of a satisfactory procedure for titanium control.

Development of procedure

Oxidation of vanadium. Solutions obtained by decomposing ilmenite conventionally by pyrosulphate fusion contain vanadium in the tetravalent state. Treatment with excess permanganate was adopted for the oxidation to vanadium(V).

Oxidation tests with 100-µg amounts of vanadium(IV) confirmed that the usual practice of oxidation at room temperature with excess of permanganate was satisfactory in pure vanadium solutions. With 30 mg of both iron(III) and titanium-(IV) present, the oxidation rate was significantly retarded. The cause was not determined but in preference to extending standing time in the cold, heating with a moderate excess of potassium permanganate (2 ml of 0.1%) was adopted. Under these conditions, heating for 15 min was required to oxidise vanadium in typical ilmenite solutions.

An excess of permanganate of more than 0.1 ml of 0.1% solution can cause slight decomposition of the BPHA reagent in the subsequent extraction step to give extractable residues which absorb at the vanadium wavelength. Selective reduction of excess of permanganate is therefore required and is conveniently obtained with sodium azide which is preferable to other reductants, *e.g.* hydrochloric acid. The temperature required for reduction to proceed at a reasonable rate results in some slight reduction of vanadium(V) if heating is prolonged after removal of the excess of oxidant. The presence of titanium contributes to this unexpected behaviour, as cooling immediately after azide addition fails to avoid the reduction loss with titanium present at the typical level of 30 mg (see Table I). For these tests the stock titanium solution was pre-treated with permanganate to remove traces of reducing impurities. Excess was destroyed with azide and excess azide decomposed by boiling.

TABLE I

EFFECT OF TITANIUM ON REDUCTION LOSS OF VANADIUM(V)

(Conditions: 100 µg of vanadium(IV) heated with excess $KMnO_4$ in 2 *M* H_2SO_4. Excess reduced with azide. Heating time varied after $KMnO_4$ removed)

Ti added (mg)	*Heating time (min)*	*Absorbance*	*Yield (%)*
Nil	Nil	0.372	100
Nil	10	0.334	90
30	Nil	0.353	95
30	10	0.331	89

Fortunately, a limited small amount of permanganate is tolerated in the BPHA extraction and the addition of a controlled amount after the azide reduction of the first excess restores quantitative oxidation of the vanadium (see Table II).

Extraction and sulphate–chloride colour conversion. Most BPHA procedures for vanadium suffer from the disadvantage that direct extraction from a mixture of sulphuric acid and 6 *M* hydrochloric acid limits the permissible sulphuric acid concentration. An equilibrium exists between sulphate and chloride forms of vanadium–BPHA complex and full conversion to chloride form is not obtained if the sulphuric acid concentration is above 1 *M*. In the proposed two-stage extraction procedure, no such limitation exists, as the sulphate form is extracted first and sulphuric acid can

TABLE II

OXIDATION OF VANADIUM(IV)

(Conditions: 100 μg of vanadium(IV), 30 mg of titanium(IV), 30 mg of iron(III), and 2 ml of 0.1% $KMnO_4$. Heating time varied; azide added and excess destroyed; standing time with 0.1 ml 0.1% $KMnO_4$ varied)

Heating time 1st oxidation (min)	*Standing time 2nd oxidation (min)*	*Absorbance*
30	30	0.370
30	0	0.344
15	15	0.374
15	5	0.374
5	5	0.360
5	2	0.315
0	30	0.349

conveniently remain at the 2 *M* concentration needed for the previous heating stage. An equal volume of 0.1% BPHA in chloroform is used to extract the vanadium complex, and without removing the aqueous phase, an equal volume of concentrated hydrochloric acid is added for the conversion to the chloride form. The chloride medium at this stage causes some further extraction of titanium–BPHA complex but the major fraction of the titanium still remains in the aqueous phase.

Removal of titanium from solvent phase. Isolation of a solvent phase containing

TABLE III

ACID CONCENTRATIONS FOR PRINCIPAL REACTIONS

Extraction H_2SO_4 (M)	*Acidity[a] HCl (M)*	*Triphosphate scrub H_2SO_4 (M)*	*Chloride re-conversion HCl (M)*	*Absorbance*
0.1	6	2	6	0.361
0.5	6	2	6	0.361
1	6	2	6	0.364
2	6	2	6	0.375
3	6	2	6	0.374
4	6	2	6	0.374
2	1	2	6	0.316
2	2	2	6	0.354
2	4	2	6	0.366
2	6	2	6	0.373
2	6	0.1	6	0.355
2	6	0.5	6	0.359
2	6	1	6	0.369
2	6	2	6	0.372
2	6	3	6	0.367
2	6	2	4	0.367
2	6	2	6	0.373
2	6	2	8	0.373
2	6	2	not used	0.364[b]
2	6	not used	not used	0.382[c]

[a] Two-stage procedure without aqueous phase removal.
[b] Extent of reversion to sulphate colour form.
[c] Cloudy.

all the vanadium and only a minor fraction of the titanium offers certain advantages for ultimate titanium elimination. Relatively high concentrations of complexing agent can be employed in an aqueous scrub to achieve complete titanium removal from the solvent phase. To determine a suitable complexing agent, a comparison of oxalate, citrate, tartrate, sulphosalicylate, orthophosphate and tripolyphosphate was made, the most effective removal of titanium being obtained with tripolyphosphate. Sulphuric acid alone was also of some benefit in titanium removal, so that a scrub medium of an 8% solution of pentasodium triphosphate (close to saturation) in 2 *M* sulphuric acid was selected. Such high acidity is necessary in any case to hold the vanadium complex quantitatively in the organic phase. The high sulphate concentration does however cause slight colour re-conversion to the sulphate form, so that a final wash with 6 *M* hydrochloric acid is required to restore quantitatively the chloride form. The absorbance is then read at 535 nm.

Tests to establish the various optimal acid concentrations throughout the procedure are summarised in Table III.

EXPERIMENTAL

Reagents

B.P.H.A. 0.1%. Dissolve 0.1 g of N-benzoyl-N-phenylhydroxylamine in 100 ml of chloroform. Prepare fresh daily.

Sodium triphosphate 10%. Use vanadium-free material. It may be necessary to prepare this from A.R. grades of sodium dihydrogen phosphate and disodium hydrogen phosphate[18].

Glass distilled water was used throughout. Analytical-reagent-grade chemicals were used wherever possible.

Procedure

To 15 g of sodium bisulphate fused in a quartz (or Vycor) flask add 1 g of the ilmenite (minus 200 mesh). For rutile, use a 0.5-g sample and 10 g of sodium bisulphate. Fuse until the sample has completely decomposed, then cool and dissolve with heating in 50 ml of 2 *M* sulphuric acid. Filter into a 200-ml standard flask, retreat the residue if necessary and dilute to volume.

Transfer a 20-ml aliquot to a 50-ml squat beaker and add 3 ml of 10 *M* sulphuric acid to provide an acidity of 2 *M* at 20-ml volume. Place on a hot plate adjusted to give a solution temperature of 95° and heat for 20 min from cold, evaporating the solution to *ca.* 20 ml. Add 2 ml of 0.1% potassium permanganate solution and heat at 95° for 15 min. Remove excess of permanganate with aqueous 1% (w/v) sodium azide solution added dropwise and boil to remove excess. Cool and transfer to a 100-ml conical separating funnel free from organic lubricants. Add 0.1 ml of 0.1% potassium permanganate and stand for 5 min.

Add 20 ml of 0.1% BPHA in chloroform and extract for 2 min. Settle, add 20 ml of 11 *M* hydrochloric acid and extract for 1 min. Settle and transfer the organic phase to a second funnel, retaining the aqueous phase. Add to the organic phase 25 ml of a solution containing 20 ml of 10% sodium triphosphate and 5 ml of 10 *M* sulphuric acid (this mixture should be used within 1 h to avoid hydrolysis) and extract for 2 min.

Settle, transfer the organic phase to a clean separating funnel, retaining the aqueous phase, and then extract it with 20 ml of 6 *N* hydrochloric acid for 1 min. Transfer to a 25-ml standard flask. Run 5 ml of 0.1% BPHA in chloroform through the three separating funnels containing retained aqueous phases, with 1-min extractions. Combine with the main solution and dilute to 25 ml with chloroform if necessary. Measure the absorbance in a 10-mm cell at 535 nm. 100 μg V$\equiv$0.372 absorbance.

RESULTS AND DISCUSSION

Calibration curve

Various amounts of vanadium ranging from 10 to 200 μg were taken through the procedure. Absorbance values were proportional to vanadium concentration to within $\pm 2\%$. Colours were stable for up to 4 h and no necessity for drying was observed.

Molar absorptivity

The absorbance obtained is equivalent to a molar absorptivity of $4.75 \cdot 10^3$ which is slightly higher than values reported in other work, *viz.* $4.56 \cdot 10^3$ [10] and $4.65 \cdot 10^3$ [12].

Ethanol effect

It has been reported[12] that the presence of ethanol added as a preservative to chloroform has a marked effect on the molar absorptivity of the vanadium complex and causes a shift in the absorption peak. To examine this aspect, various amounts of ethanol were added to purified re-distilled chloroform. It was noted that ethanol is rapidly transferred to the aqueous phase in the procedure and no evidence of any effect on the final colours could be obtained. Unpurified a.r. chloroform is therefore a satisfactory reagent in the proposed procedure.

Recovery

To a synthetic ilmenite solution prepared from high-purity materials and checked for blank, various amounts of vanadium ranging from 10 to 200 μg were added. With respect to the procedure aliquot, these amounts represent 0.02 to 0.4% V_2O_5 in the ilmenite. Recoveries were quantitative to $\pm 2\%$.

No temperature effects were observed when the complete procedure was used with a synthetic matrix over the range 15°–30°. A B.C.S. standard steel was also analysed by the same procedure, with results as in Table IV.

TABLE IV

VANADIUM DETERMINATION IN STEEL BCS SS17

Certificate value (%)	*Found (%)*
0.097, 0.102, 0.106, 0.107, 0.109, 0.111	0.106, 0.106

Interferences

Certain unusual features of the proposed procedure contribute to the satisfactory elimination of titanium interference. The triphosphate complexing agent cannot be added to the original solution before extraction of vanadium, because the chloride system favours increased stability of the titanium–BPHA complex. Adequate control is obtained through the scrub treatment of a phase containing a decreased proportion of the titanium. This procedure also avoids the formation of cloud in the solvent phase.

In the re-extraction of original solution to obtain quantitative vanadium recovery, the titanium loading on the system is further minimised by not combining the second solvent phase with the main vanadium stock until it has been taken through the "waste liquors" retained in the original separating funnels.

Chromium at levels similar to vanadium is without interference in the procedure, but high-chrome ilmenites containing for example 0.5–5% Cr_2O_3 require a modified procedure. Selective reduction is inadequate as both chromium(VI) and chromium(III) interfere at such levels. After oxidation to obtain all the chromium in the hexavalent state a simple preliminary extraction with methyl isobutyl ketone in 1 M hydrochloric acid medium removes chromium[19]. Evaporation of the raffinate to fumes with sulphuric acid provides a satisfactory sample for the proposed procedure.

Sodium triphosphate reagent

One commercial product, laboratory reagent grade, was found to contain 10 p.p.m. vanadium. Byusing A.R. reagents for a laboratory preparation of triphosphate, a material containing less than 0.5 p.p.m. was obtained.

Alternative vanadium reagents

Since the introduction of BPHA, several alternative reagents of similar structure have been proposed. Among these are N-furoylphenylhydroxylamine[16], N-benzoyl-*o*-tolylhydroxylamine[20,21] and N-cinnamoyl-N-phenylhydroxylamine[22]. Increases in sensitivity of up to 30% were observed with these reagents, but no other advantages appeared to be evident. Titanium interfered with the furoyl and cinnamoyl compounds but good titanium tolerance was obtained with the N-benzoyl-*o*-tolyl reagent by reading the absorbance at 550 nm. Unfortunately this reagent showed inferior performance against chromium. Taking availability of reagents into account, the original N-benzoyl-N-phenylhydroxylamine can be regarded as an adequate reagent.

Sensitivity increase for upgraded ilmenite and synthetic rutile

The procedure developed removes interference from 30 mg of titanium and conveniently determines as little as 0.005% V_2O_5. For V_2O_5 contents down to 0.001%, it is desirable to double the aliquot. Control of the extra titanium (60 mg total) is obtained by doubling the extraction time of the triphosphate scrub to 4 min and doubling the reconversion time in the final hydrochloric acid scrub to 2 min.

SUMMARY

A new procedure has been developed for eliminating interference from titanium in the N-benzoyl-N-phenylhydroxylamine procedure for determination of vanadium. After the oxidation of vanadium(IV) with potassium permanganate,

vanadium(V)–BPHA complex is extracted into chloroform from sulphuric acid and converted to the chloride form before removal of the original aqueous phase. Co-extracted titanium is removed from the isolated organic phase by extracting with a solution of pentasodium tripolyphosphate in 2 *M* sulphuric acid. Appropriate arrangement of the order of reagent addition avoids reduction of vanadium(V) in the strongly acidic chloride systems.

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SOME CONSIDERATIONS ON APPARENT DEVIATIONS FROM LAMBERT–BEER'S LAW

K. BUIJS AND M. J. MAURICE
Euratom, European Institute for Transuranium Elements, Karlsruhe (Germany)
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In absorption spectroscopy the proportionality between absorbance and concentration of absorbing species is expressed by Beer's law. A similar relationship exists between the integrated intensity of an absorption band and the concentration of absorbing species. In a certain number of cases, however, it is found that this law is not obeyed, *i.e.* the relationship between absorbance or integrated intensity and concentration is found not to be linear. The absorbance is not proportional to the concentration more often than the integrated intensity. For practical reasons, however, in the spectrophotometric determination of an unknown concentration, the absorbance is used rather than the integrated intensity.

Theoretically no argument exists against the validity of Beer's law, nor against Lambert's law, which relates absorbance to optical path length. Both laws are assumed to be basically valid and any deviation is considered as an apparent deviation.

Three kinds of effects can be distinguished which may cause these apparent deviations:

(*a*) chemical and/or physical (non-instrumental) effects, such as a chemical equilibrium determining the concentration of the absorbing species or physical interactions affecting the absorbing complexes or molecules;

(*b*) instrumental effects, such as the lack of proportionality between detector response and light intensity or the fact that for sharp absorption bands the peak height is a function of the spectral slit width;

(*c*) a combination of the effects mentioned above.

These effects will further be called effects of the first, the second, and the third type respectively.

Effects of the first type are inherent to the system studied and can only be changed by changing the system. Effects of the second type—on the other hand—can be eliminated by using adequate measuring equipment. However, in many cases instrumental limitations have to be accepted, *e.g.* for economic reasons.

In this paper the characteristics and consequences of the different types of apparent deviations from Lambert–Beer's law will be studied more closely, in order to define the limits they place upon application of absorption spectroscopy for analytical and physico-chemical studies.

CRITERIA FOR THE DISTINCTION BETWEEN FACTORS CAUSING DEVIATIONS FROM LAMBERT–BEER'S LAW

An apparent deviation caused by effects of the first type implies that for the real absorbance, E', of the system instead of the relation

$$E' = \mathrm{a}\, C\, l \tag{1}$$

one finds

$$E' = \mathrm{a}\, C\, l + \mathrm{b}\, C^2\, l + \ldots + \mathrm{g}\, C^m\, l \tag{2}$$

where C = concentration, l = cell length, and a, b ... g = constants.

In the absence of instrumental limitations, the measured absorbance, E, is equal to the real absorbance, E':

$$E = E' \tag{3}$$

However, if instrumental effects play a role, the real absorbance is not recorded by the instrument. The measured absorbance, E, can then be related to the real absorbance, E', in first approximation by

$$E = E' + \mathrm{p}\, E' + \mathrm{q}\, E'^2 + \ldots + \mathrm{z}\, E'^n \tag{4}$$

where p, q ... z are constants.

It should be remarked that a different non-linear relationship between E and E' does not affect the conclusions discussed below.

The four possible combinations of eqns. (1) and (2) on the one hand and eqns. (3) and (4) on the other hand, give rise to four different relations between E, C and l, which permit a distinction between them.

(*a*) Substitution of eqn. (1) in eqn. (3) gives

$$E = \mathrm{a}\, C\, l \tag{5}$$

No deviations from linearity occur. This case is not discussed any further.

(*b*) Substitution of eqn. (2) in eqn. (3) gives

$$E = \mathrm{a}\, C\, l + \mathrm{b}\, C^2\, l + \ldots + \mathrm{g}\, C^m\, l \tag{6}$$

The measured absorbance at a given concentration is proportional to the cell length, l. This means that for analytical purposes one calibration equation of the form

$$E/l = \mathrm{a}\, C + \mathrm{b}\, C^2 + \ldots + \mathrm{g}\, C^m \tag{7}$$

is sufficient to deal with all combinations of C and l. This is the case where effects of the first type cause the deviations.

(*c*) Substitution of eqn. (1) in eqn. (4) gives

$$E = \mathrm{a}\, C\, l + \mathrm{p}\, \mathrm{a}\, C\, l + \mathrm{q}\, \mathrm{a}^2\, C^2\, l^2 + \ldots + \mathrm{z}\, \mathrm{a}^n\, C^n\, l^n \tag{8}$$

This equation is valid when deviations are caused by effects of the second type. The measured absorbance is no longer proportional to either concentration or cell length, but depends only on the product of concentration and cell length. If we now put

$$Q = C\, l \tag{9}$$

a calibration equation of the form

$$E = \mathrm{A}\,Q + \mathrm{B}\,Q^2 + \ldots + \mathrm{G}\,Q^n \tag{10}$$

is found, where A, B ... G are constants. The conversion of absorbance measurements made with different cell lengths is then not made directly by transforming the measured E-value into E/l as in the case of eqn. (7), but by transforming the Q-value obtained into the appropriate C-value. Thus, also in this case, one calibration equation can be used for the evaluation of unknown concentrations from absorbances measured in cells of different lengths.

(*d*) An equation for the situation in which effects of the third type play a role is found by substitution of eqn. (2) in eqn. (4):

$$\begin{aligned}E = {} & (1+\mathrm{p})l(\mathrm{a}\,C + \mathrm{b}\,C^2 + \ldots + \mathrm{g}\,C^m) + \mathrm{q}\,l^2(\mathrm{a}\,C + \mathrm{b}\,C^2 + \ldots + \mathrm{g}\,C^m)^2 + \ldots \\ & + \mathrm{z}\,l^n(\mathrm{a}\,C + \mathrm{b}\,C^2 + \ldots + \mathrm{g}\,C^m)^n\end{aligned} \tag{11}$$

This equation is not linear in either l or C. In contrast to eqn. (10), it contains a number of terms such as $\mathrm{b}\,l\,C^2$, which are inhomogeneous in l and C. As a consequence there is no simple way to relate absorbance measurements made in a l-cm cell to those made in a l'-cm cell. For each cell length separate calibration graphs have to be drawn up.

To summarize, it can be said that the deviations are caused by effects of the first type when the ratio E/l is constant for each C-level, and by effects of the second type when the product $C\,l$ is constant for each E-level. This means that when E/l is plotted *vs.* C or when $C\,l$ is plotted *vs.* E, one single curve should be obtained. If no single curve is found in either of the two cases, deviations are caused by effects of the third type.

The cases (*a*) and (*b*) are those usually found in ultraviolet and visible spectroscopy. The behaviour described in cases (*c*) and (*d*) is shown very often by sharp absorption bands in infrared spectroscopy, as well as in visible spectroscopy by the absorption bands of the lanthanide and actinide ions.

A number of measurements on cobalt(II)- and plutonium(VI) solutions have been made to illustrate the distinctions made above.

EXPERIMENTAL

Absorbance measurements were made with a Beckman DK 2A spectrophotometer on the following systems:

I. a cobalt(II) solution which was 0.5 *M* in ammonium sulphate and 0.01 *M* in EDTA and was at pH 3;

II. a plutonium(VI) solution which was 4 *M* in nitric acid;

III. plutonium(VI) solutions which were 0.05–0.5 *M* in sulphuric acid;

IV. a plutonium(VI) solution which was 2 *M* in sulphuric acid.

Cell lengths used were 1, 2, 5 and 10 cm. Metal ion concentrations were also chosen in the ratios 1:2:5:10. Throughout the measurement of each series, the slit width of the spectrophotometer was kept constant. The absorbance of the sharp plutonium(VI) peak was measured by the base-line technique described in an earlier paper[1]. The reference solutions contained all the solutes, the concentration of which was constant in each series. Absorbance measurements were performed at the wavelength of maximum absorptivity. Results are given in Table I.

TABLE I

ABSORBANCE MEASUREMENTS ON COBALT(II) AND PLUTONIUM(VI) SOLUTIONS UNDER DIFFERENT CONDITIONS

System	*Metal ion concentration C (mg/l)*	*λ_{max} (nm)*	*Absorbance (E) measured in cell of l cm*			
			l = 1	*l = 2*	*l = 5*	*l = 10*
I, Co(II)	3.15	510				0.183
	6.30				0.150	0.293
	15.75			0.111	0.276	0.559
	31.50		0.082	0.172	0.437	0.860
II, Pu(VI) in 4 M HNO_3	10.9	831				0.125
	21.8				0.130	0.240
	54.5			0.128	0.292	0.548
	109		0.131	0.236	0.550	0.950
III, Pu(VI) in H_2SO_4	12 0.05 M H_2SO_4	833				0.145
	24 0.10				0.141	0.268
	60 0.25			0.129	0.303	0.575
	120 0.50		0.107	0.210	0.521	0.987
IV, Pu(VI) in 2 M H_2SO_4	12	834				0.122
	24				0.119	0.236
	60			0.115	0.305	0.626
	120		0.110	0.225	0.563	1.071

DISCUSSION

In Table I the apparent deviations from Lambert–Beer's law are easily seen in the rows and columns respectively. In order to obtain more detailed information about the system studied, the criteria discussed above will now be applied.

System I. To the measurements listed in Table I for system I the test supplied by eqn. (7) is applied. The measured absorbances are divided by the corresponding cell length. The resulting E/l values are given as a function of the corresponding C-values in Table II, from which it can be seen that for each C-level, E/l is constant within experimental error, which means that the system is described by eqn. (7). This is in agreement with the fact that the broad band of cobalt(II) in the solutions studied should be immune to slit width effects. However, simultaneous formation of sulphato- and EDTA-complexes provides a chemical basis for apparent deviations from Lambert–Beer's law.

TABLE II

VALUES OF E/l AS A FUNCTION OF C FOR SYSTEM I

Co(II) concentration (mg/l)	*E/l*			
	l = 1 cm	*l = 2 cm*	*l = 5 cm*	*l = 10 cm*
3.15				0.0183
6.30			0.0300	0.0293
15.75		0.0555	0.0552	0.0559
31.50	0.0820	0.0860	0.0867	0.0860

System II. The results obtained with this system (Table I) are inconsistent with eqn. (7), as is readily verified. However, when values for $Q = C\,l$ are calculated from Table I and these are plotted against the corresponding E-values, the points lie on one curve, which means that for plutonium(VI) in 4 M nitric acid a calibration graph can be constructed of the type represented by eqn. (10). The apparent deviations from Lambert–Beer's law, therefore, are due to the nature of the measurement of the sharp plutonium(VI) absorption peak and not to chemical effects.

System III. The absorbance values obtained with solutions of varying concentrations of plutonium(VI) and sulphuric acid as listed in Table I cannot be reconciled with eqn. (7), nor with eqn. (10). It follows then, that we are dealing with a system the behaviour of which can be described by eqn. (11). The measurement of the sharp plutonium(VI) absorption band provides the instrumental factor, which combines with a chemical factor, *viz.* varying degrees of complexation, to cause apparent deviations from Lambert–Beer's law.

System IV. The absorbances measured on plutonium(VI) in 2 M sulphuric acid very nearly obey eqn. (7), as can be seen from Table III where the E/l values are given as a function of the corresponding C-values. This means that for this system the influence of effects of the second type is small compared to those of the first type (complex formation). This different behaviour of system IV compared to systems II and III can be attributed to an effect of broadening of the plutonium(VI) absorption band as a result of the formation of higher sulphato complexes of plutonium(VI). Here, the chemical effects influence the instrumental effects.

TABLE III

VALUES OF E/l AS A FUNCTION OF C FOR SYSTEM IV

Pu(VI) concn. (mg/l)	*E/l*			
	l = 1 cm	*l = 2 cm*	*l = 5 cm*	*l = 10 cm*
12				0.0122
24			0.0238	0.0236
60		0.0575	0.0610	0.0626
120	0.1100	0.1125	0.1126	0.1071

With the aid of the considerations described above, it is possible to obtain more detailed information on a system studied and to determine the type of apparent deviation from Lambert–Beer's law shown, by the system. By doing so while setting up a spectrophotometric procedure, one can obtain much information about the experimental changes required to arrive at the optimum conditions of analysis. In this respect the independence of cell length which characterizes the calibration eqns. (7) and (10) is of special interest. It is possible in this way to check if absorbance measurements, made in cells of different lengths, can be represented as a function of concentration by one equation. Then, moreover, it can be decided whether one should plot E/l against C, or $C\,l$ against E.

SUMMARY

Apparent deviations from Lambert–Beer's law may be caused by chemical and/or physical effects, instrumental effects or both. A general procedure is described for distinguishing between these three types of effects. The validity of the procedure is verified by some measurements in the visible region of the spectrum on cobalt(II)- and plutonium(VI) solutions. The method is shown to be especially valuable for establishing the correlation between absorbance data, measured with different cell lengths.

RÉSUMÉ

Les déviations apparentes par rapport à la loi de Lambert–Beer peuvent avoir des causes chimiques et/ou physiques, des causes instrumentales ou les deux. On décrit une méthode générale qui permet de distinguer entre les trois types de causes. La validité de la méthode est vérifiée par quelques mesures dans la région visible du spectre sur des solutions de cobalt(II) et de plutonium(VI). On montre que la méthode est particulièrement indiquée pour trouver la relation entre les valeurs de la densité optique, mesurées avec des cellules de longueurs différentes.

ZUSAMMENFASSUNG

Scheinbare Abweichungen vom Lambert–Beerschen Gesetz können durch chemische und/oder physikalische Faktoren, instrumentelle Faktoren oder einer Kombination beider Arten von Faktoren verursacht werden. Eine allgemeine Methode zur Unterscheidung zwischen diesen drei Typen von Ursachen wird beschrieben. Die Gültigkeit der Methode wird kontrolliert durch einige Messungen im sichtbaren Gebiet des Spektrums, und zwar an Cobalt(II)- und Plutonium(VI) Lösungen. Es wird gezeigt, dass die Methode besonders geeignet ist, um die Beziehung zwischen Extinktionsdaten, die in Zellen verschiedener Länge gemessen wurden, festzustellen.

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ION-SELECTIVE ELECTRODES IN CONTINUOUS-FLOW ANALYSIS

DETERMINATION OF CALCIUM IN SERUM

J. RŮŽIČKA* AND J. C. TJELL
Chemistry Department A, Technical University of Denmark, Building 207, Lyngby (Denmark)

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Since the glass electrode became generally used for pH measurements, many investigations have been made to develop electrodes which could measure the activity of other ions in solution. However, only recently when solid-state electrodes and liquid–liquid membrane electrodes were developed, has the reproducibility of this technique become sufficient for analytical purposes. Now the number of available sensors is increasing so rapidly that reviewers do not feel competent to give a complete account[1]. Although perhaps the fluoride electrode is the most popular one (either solid state[2] or Pungor type[3]), other electrodes suitable for sodium, potassium, chloride, bromide, iodide, cadmium, calcium, copper, zinc, lead, silver, cyanide, fluoroborate, nitrate, perchlorate and thiocyanate ion activity measurement are now produced by a single manufacturer[2]. All of them exhibit Nerstian potential behaviour down to the limit of detection[4]:

$$E = E_0 + 2.3\,\frac{RT}{nF}\log\left(a_{\mathrm{M}^{n+}} + \sum K_i\, a_i^{2/Z_i}\right) \tag{1}$$

where E is the electrode potential, E_0 is the potential of the electrode at standard condition, $2.3\,RT/nF$ is Nernst potential factor, M^{n+} is the test ion, K_i and Z_i are the selectivity ratios and charges of other ions in solution, and a_i denotes the ionic activities.

The limit of detection is fairly low and as little as 10^{-5} moles/l of calcium, chloride, sodium, fluoroborate, nitrate, perchlorate and thiocyanate, $10^{-6}M$/l of bromide, cyanide, fluoride and zinc, $10^{-7}M$/l of cadmium and $10^{-8}M$/l or less of copper, iodide, lead, silver and sulfide can be determined by Orion electrodes[2]. Above this limit there is a change of potential of 59.2 mV for monovalent and 29.6 mV for divalent ions when their activity rises or decreases ten times (at 25°). In cases when concentration is of analytical interest, a calibration curve is prepared with a series of standards, the composition of which must be identical with that of the test samples. When this is not possible any differences in ionic strength, pH, content of complexing agents, temperatures, etc., must be taken into account. The *slope* of the calibration curves obtained in this way usually does not change from day to day, but the electrode potential changes considerably, because the E_0 depends on the age of the electrode, the

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* On leave from: Department of Nuclear Chemistry, Faculty of Nuclear Physics, Prague 1, Brehova 7, Czechoslovakia.

stirring rate, the depth of immersion, etc., and therefore frequent recalibration is recommended[5-7].

In continuous-flow analysis all samples are treated identically and all reaction and measurement conditions can be strictly controlled. A large number of test and standard samples can be analysed automatically; the baseline is easily controlled and readjusted. Mainly for these reasons, AutoAnalyzer methods are now widely applied in clinical chemistry, soil chemistry, industry and in other areas; colorimetric, fluorimetric, atomic-absorption, flame-photometric, thermometric and even polarographic methods of completing determinations have been used[8-10].

The applicability of both potentiometric measurements and continuous-flow analysis to a variety of analytical problems and the fact that the drawbacks of the first technique can be overcome by the advantages of the second, makes their combination especially attractive. The present work is aimed at the experimental verification of this idea.

EXPERIMENTAL

Apparatus

The apparatus was constructed according to the given manifold (Fig. 1) from Technicon Sampler II, Proportioning Pump II, Radiometer 26 pH meter, and Recorder RE 520 (Servogor Goertz Electro). Pump tubes, coils, pulse suppressor, etc., were standard Technicon materials.

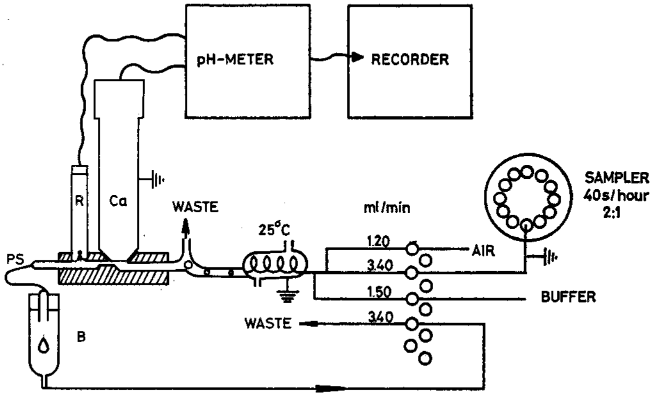

Fig. 1. Automated determination of calcium by means of the ion-sensitive electrode. (Ca) calcium ion electrode, (R) calomel electrode, (PS) a pulse suppressor, (B) bubble chamber.

Electrodes. Calcium ion electrode model 92-20, Orion (Massachusetts). Reference electrode calomel model K 401 Radiometer (Copenhagen).

Flow cell. This was made of Teflon block (Fig. 1) and mounted together with the electrodes on a chemical stand. The whole assembly was tilted as much as possible to prevent air bubbles (which might eventually enter the cell) becoming trapped under the electrodes.

Reagents and standards

Reagents were prepared from analytical-grade reagents and deionized double-distilled water. For the lowest concentrations of calcium (Fig. 2), Suprapur Merck chemicals were used.

Buffer solution. This was prepared by mixing 1 l of 0.02 *M* ammonium chloride with 5 ml of 1 *M* aqueous ammonia. When this buffer was used in the analysis of samples with very low calcium contents (Fig. 3), *ca.* 0.01 g of sodium diethyldithiocarbamate was added to 1 l of the buffer to mask traces of Zn, Pb and other heavy metals, because K_1 for Zn^{2+}, Pb^{2+} and Cu^{2+} was reported to be 2.2, 0.63 and 0.27[2]. In the case of serum analyses the ammonium chloride buffer was made 0.135 *M* with respect to sodium chloride in order to avoid variations in ionic strength and sodium content.

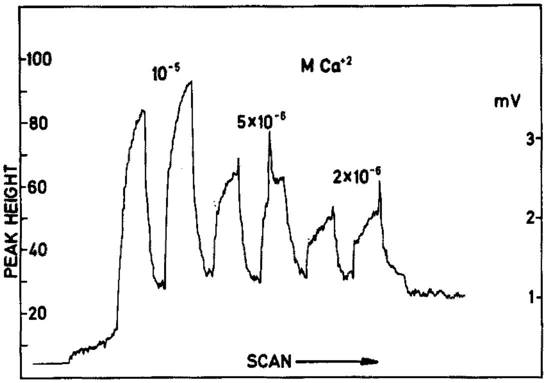

Fig. 2. Maximum sensitivity of the method. The drift of the baseline and adsorption of calcium on tubing (the first peak is lower than the second one) are the limiting factors. 20 samples/h.

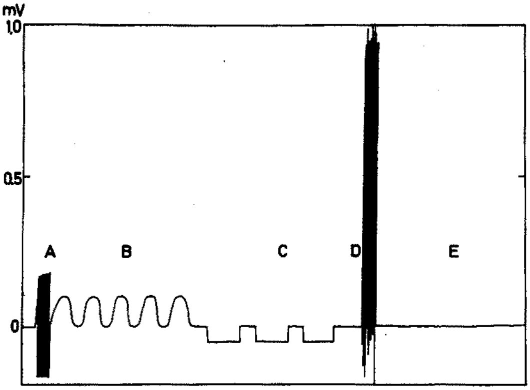

Fig. 3. Influence of different factors on the stability of the baseline. (A,C) static electricity produced by pump, (B) pressure changes in the flow cell, (D) air bubbles in the flow cell, (E) a normal baseline.

Wash. The wash solution was 10^{-4} *M* hydrochloric acid. For serum analysis, this solution also contained 0.135 *M* sodium chloride and $1 \cdot 10^{-5}$ *M* calcium(II).

Calcium standards. These were prepared from a standardized stock solution of calcium chloride in 10^{-4} *M* hydrochloric acid by further dilution with 10^{-4} *M* hydrochloric acid. For serum analyses all standards were made 0.135 M in sodium chloride.

Titrisol standards. These Merck standards contain, besides calcium also 3.30 g Na, 0.150 g K and 0.020 g Mg per l. These were diluted according to the manufacturer's instructions but with hydrochloric acid so as to be finally also 10^{-4} M with respect to hydrochloric acid.

Seronorm. These human serum standards (Nyegård & Co., Oslo) were dissolved in 10.00 ml of redistilled water and immediately analysed. The prepared samples correspond to undiluted normal human serum, the *total* calcium content corresponding to $2.6 \cdot 10^{-3} M$ as found by compleximetric titration, flame photometry, colorimetry and atomic absorption. These samples, however, gave always about 5% higher reading for the first and about 2% higher reading for the second sample than the average value for a series of samples of identical composition. This systematic error was avoided by diluting dissolved Seronorm standards with an equal volume of 0.135 M sodium chloride.

Horse serum. This was diluted 1:1 with 0.135 M sodium chloride, because similar carryover as in the case of human serum was observed.

Measurement under static conditions

The response of the electrode to calcium and hydrogen ion activities as well as the reproducibility of measurement and ageing were found to be the same as reported by the manufacturer[2] and by other authors[4,5,7,11-14].

Measurement under flow conditions

Interaction between the pump and the electrodes was observed and found to be due to static electricity and changes of pressure. The electrical interference was characteristically pronounced on the baseline (Fig. 3,A) and was synchronized with the movement of the rollers in the pump. As it was caused by static electricity produced by the pumping action, it was found possible to avoid it by proper earthing of the instruments and of the manifold parts (see Fig. 1) and by using a bubble chamber, which provided electrical insulation between the pump and the flow cell. Also the calcium electrode had to be wrapped in aluminium foil and earthed. The pressure changes in the flow cell also influenced the baseline (Fig. 3,B); this could be avoided by means of the bubble chamber, by the pulse suppressor (which is a piece of the standard tubing of 0.03-in internal diameter and 10-in length), and by letting the liquid drop freely from the debubbler into the waste line which had a large diameter.

The baseline was found to drift when $2 \cdot 10^{-6}$ M Ca^{2+} to 10^{-5} M Ca^{2+} was analysed (Fig. 2). For higher contents (Fig. 4) this drift was found to be smaller and associated with changes of ambient temperature and with the equilibrium concentration of calcium in the flowing stream during washing periods. The latter factor was stabilized by making a wash solution containing 10^{-5} M calcium(II) (Fig. 5). This and the simple thermostating of the solutions before they entered the flow cell resulted in a reasonable baseline which was only slightly affected by changes in room temperature. This could be avoided by thermostating the flow cell and the electrodes or by electronic readjustment of the baseline.

Calibration curves (Figs. 4 and 5) were constructed as usual in AutoAnalyzer methods with ammonium chloride buffer, 10^{-4} M hydrochloric acid as wash and

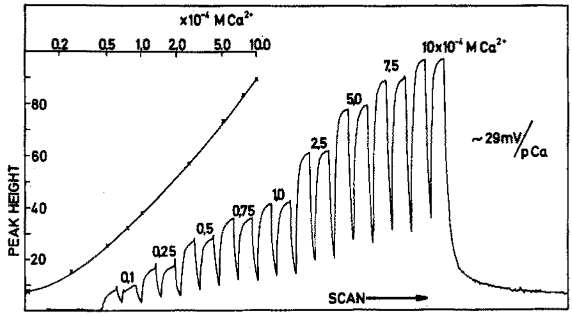

Fig. 4. Calibration record in absence of sodium chloride. The points of the calibration graph (×) are the mean values of two measurements. 40 samples/h.

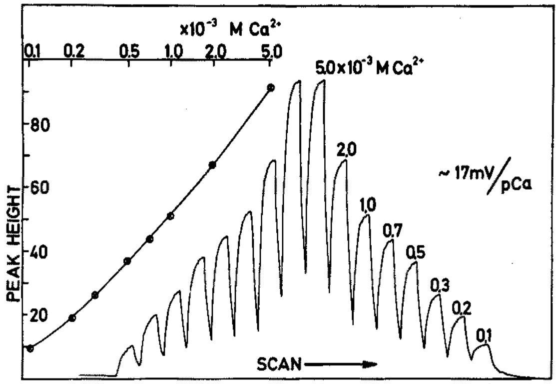

Fig. 5. Calibration record for serum analysis (in presence of NaCl). There is nearly no carryover at this sampling rate (40 samples/h) as the points for increasing concentrations × are close to those for decreasing concentrations (o).

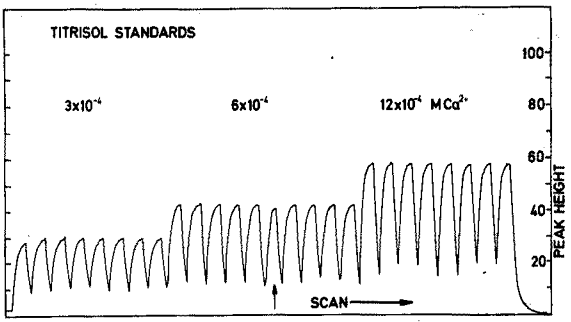

Fig. 6. Repetitive analyses of Merck Titrisol standards. 40 samples/h. The arrow indicates the sample which, by mistake, was inspired for a shorter period than the other ones.

calcium standards in 10^{-4} *M* hydrochloric acid. In the absence of sodium chloride (Fig. 4), the slope of the calibration curve was close to the theoretical value. In the presence of sodium chloride, the slope was found to be only about 17 mV per tenfold change of the calcium concentration which means that the electrode is not specific for calcium as sodium ions contribute to the electrode potential (eqn. 1). The influence of hydrogen ions was negligible because pH 8.4 ±0.1 was maintained in all experiments. This observation is in agreement with the measurements under static conditions, as well as with the fact that the slope of the calibration graph changes only a little from day to day[4,5,7]. One standardization daily and a check with two standards after a series of about forty samples was therefore satisfactory.

Carryover from sample to sample was evaluated in the usual way[15]. It was found that the half-wash time was about 14 sec with a lag phase below 2 sec. From this it follows [15] that with a sampling rate of 20 samples/h, no interaction between the samples should occur. There will be only 2% interaction for 40 samples/h and approximately 7% interaction for a sampling rate of 60 samples/h. This can also be seen from Figs. 5 and 6 where practically no carryover was observed at a sampling rate of 40 samples/h. It is difficult to decide to what extent this factor is due to the dynamic response of the calcium electrode and to the actual cross-contamination of subsequent samples. A dynamic study of the electrode response has shown that a 33% change in pCa is registered[5] within 6 sec. It appears therefore that the present carryover is composed of both factors because the theoretical half-wash time due to the electrode response would be 9 sec only.

RESULTS AND DISCUSSION

The reproducibility of the determination can be seen from Fig. 6 and from Table I. The small positive deviation between the true (t) and the observed calcium content ($\bar{x}$) of Titrisol standards is probably due to incorrect reading of the baseline because the error decreases with increasing calcium content. The precision of analysis of Seronorm standards of human serum is lower than that of Titrisol standards, but it compares favourably with the AutoAnalyzer colorimetric procedure (s±3.9 and ±1.9)[16]. Unfortunately, the content of ionized calcium in Seronorm standards is unknown, but it is recognized that the content of ionized calcium in a fresh normal serum lies between 36 and 46% of the total calcium content, depending on how the

TABLE I

REPRODUCIBILITY OF THE PROPOSED METHOD[a]

Sample	*Calcium content* *(t)·10⁻⁴M/l*	*Calcium found* *($\bar{x}$)·10⁻⁴M/l*	*Standard deviation* *of a single measurement* *s(%)*	*of the mean* *$\bar{s}$(%)*	*$\bar{x}$/t* *(%)*
Titrisol	3.000	3.080	± 1.9	± 0.63	102.5
Titrisol	6.000	6.083	± 0.25	± 0.09	101.4
Titrisol	12.000	12.021	± 0.45	± 0.25	100.2
Seronorm[b]	13.00[c]	4.250[d]	± 2.18	± 0.84	32.7
Seronorm[b]	13.00[c]	4.300[d]	± 2.15	± 1.66	33.0

[a] t = true value; $\bar{x}$ = mean of observed values; $s = [\Sigma(x_i - x)^2]/(n - 1)^{\frac{1}{2}}$; $\bar{s} = s\,n^{-\frac{1}{2}}$.
[b] Two different samples from the same batch, both diluted 1 : 1 with 0.135 *M* NaCl. Sample I: five measurements. Sample II: three measurements.
[c] Total calcium.
[d] Unbound (ionized) calcium.

serum was treated before analysis. The small difference between the two values obtained by analysing two different Seronorm samples from the same batch indicates good accuracy in the present method. The decision if the *ionized* or *total* calcium should be routinely determined in human serum lies beyond the scope of this paper. However, it should be noted that it has been long recognized that only ionized calcium is involved in biochemical processes such as excitation, conduction, membrane phenomena, muscle contraction and relaxation, etc.[7]. The reason why the total calcium content is usually determined is that routine methods based on ultrafiltration or dialysis and subsequent colorimetry, flame photometry, etc., are unable to distinguish between total and ionized calcium content.

The selectivity of determination depends on the selectivity of the calcium electrode, which has already been discussed by various authors[2,4,5,11–14]. It is surely satisfactory for determining calcium in such samples as human serum which contains interfering elements (Zn, Fe, Cu) in considerably lower quantities than calcium. Furthermore, the strict control of sample composition and acidity as imposed in the AutoAnalyzer, minimizes the interference of sodium and hydrogen ions by keeping their activities at a constant level. However, for the analysis of other samples of less uniform composition than biological fluids, the selectivity of calcium electrodes should be further evaluated. The data and the selectivity concepts as discussed by RECHNITZ AND SHATKAY[5,11–14] are, although diverse, very interesting and useful. We believe, however, that a combination of the Henderson and Planck liquid junction equations, and of the theory of metal chelate solvent extraction, would further contribute to the theory of liquid–liquid membrane electrodes. It might also lead to a wider choice of ion-sensitive electrodes, the selectivity of which it would be possible to evaluate directly from the extraction constants of corresponding metal chelates. We hope to return to this subject in a future paper.

The combination of the AutoAnalyzer with the calcium electrode gives a method which is simpler and easier to operate than other types of sensors used for the same purpose[8,9]. Fewer reagents are used than in colorimetry[16], and the cost of a sensor is only a fraction of that of equipment for atomic absorption or flame photometry. The range, which can vary from 10^{-1} to 10^{-5} M calcium(II), is simply chosen by recorder input sensitivity and by the change of calcium content in the wash.

Other electrolytes could also be determined in serum in a similar manner, some of them, such as sodium and chloride even simultaneously in one flowing stream, with the same reference electrode.

SUMMARY

The use of a calcium-selective electrode as a sensor in procedures involving the AutoAnalyzer is described. The influence of various parameters such as temperature, pH, ionic strength, and carry-over, as well as interactions between the pump and electrodes, were studied. Quantities of calcium between $2 \cdot 10^{-6}$ and $1 \cdot 10^{-2}$ M/l were determined in synthetic aqueous samples, Merck standards for serum analysis, Seronorm standards of human serum, and non-standardized horse serum at a rate of 40 samples/h. The method was found to be simpler than colorimetry and also avoids dialysis, giving values of "free" calcium (calcium ion activity), which is clinically important.

RÉSUMÉ

On décrit l'utilisation d'une électrode sélective-calcium dans des procédés avec "autoanalyseur". On examine l'influence de divers paramètres tels que température, pH, force ionique, interactions entre pompe et électrodes. Des quantités de calcium de l'ordre de $2 \cdot 10^{-6}$ à $1 \cdot 10^{-2}$ M/l ont pu être dosées dans divers échantillons: étalons en milieu aqueux, étalons Merck pour analyse du sérum, et sérum. On peut ainsi déterminer facilement des teneurs en calcium libre, ce qui est cliniquement plus important que les teneurs en calcium total.

ZUSAMMENFASSUNG

Es wird die Anwendung einer calciumselektiven Elektrode als Anzeige bei der Verwendung eines AutoAnalyzer beschrieben. Der Einfluss verschiedener Parameter wie Temperatur, pH-Wert, Ionenstärke und apparative Eigenschaften wurde untersucht. Calciummengen zwischen $2 \cdot 10^{-6}$ und $1 \cdot 10^{-2}$ M/l wurden in synthetischen wässrigen Proben und verschiedenen Standardseren mit einer Geschwindigkeit von 40 Proben/Std. bestimmt. Die Methode ist einfacher als die kolorimetrische, vermeidet die Dialyse und ergibt Werte für die Calciumionenaktivität, welche klinisch bedeutsamer ist als der Gesamtcalciumgehalt.

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EFFECT OF ACETATE BUFFER ON THE POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANUM USING A LANTHANUM FLUORIDE MEMBRANE ELECTRODE

TORBJÖRN ANFÄLT AND DANIEL JAGNER
Department of Analytical Chemistry, University of Gothenburg, S-402 20 Göteborg 5 (Sweden)

(Received June 12th, 1969)

The potentiometric titration of fluoride with a fluoride selective membrane electrode (Orion Research Inc.) was first studied by LINGANE[1,2]. Lanthanum and thorium nitrates and $CaCl_2$ were used as titrants and lanthanum nitrate was found to be superior. Using LINGANE's titration data, ANFÄLT *et al.*[3] attempted to explain the form of the experimental titration curves by means of equilibrium calculations using the computer program HALTAFALL[4]. When fluoride was titrated with lanthanum nitrate in a medium buffered with acetate, it was not, however, possible to explain LINGANE's data even if mixed complexes, *e.g.* $LaFAc^+$, were introduced into the calculation. Nor did the equivalence volume, evaluated by means of the inflexion point and the GRAN[5] method, agree with the total concentrations of lanthanum and fluoride quoted by LINGANE. By assuming a different total fluoride concentration it was, however, possible to obtain a good fit between the calculated and experimental data by means of the stability and solubility constants used to interpret the titration data obtained in the absence of acetate. In addition it was necessary to use a somewhat high value for the formation constant of the mixed complex $LaFAc^+$ (Table V in ref. 3). This rather unsatisfactory situation called for a more detailed investigation of the lanthanum–fluoride–acetate system.

EXPERIMENTAL

Reagents

Stock solutions of *fluoride* and *nitrate* were prepared by dissolving their sodium salts (Merck p.a.) in doubly distilled water. The standard *lanthanum* solution, prepared by dissolving $La(NO_3)_3 \cdot 6H_2O$ (Merck p.a.) in doubly distilled water, was standardized against the standard fluoride solution, good agreement being obtained with the dissolved weight of lanthanum nitrate. The standard *acetate* solution was prepared by dissolving crystallized sodium acetate (Merck p.a.) in weighed amounts of acetic acid (Merck p.a.) to give a molar ratio of 1:1 and then diluting the solution with doubly distilled water. The presence of possible fluoride impurities in the standard acetate solution was checked by a potentiometric titration of 150 ml of 0.00285 M standard sodium fluoride with v ml of 0.0100 M thorium nitrate in the presence of an initial concentration of acetic acid and acetate of 0.8 M. The thorium nitrate solution used in this titration was prepared by dissolving $Th(NO_3)_4 \cdot 4H_2O$ (May and Baker p.a.) in doubly distilled water. The equivalence point, determined by the GRAN method[3,5] was 10.70 ml. Since the expected value is 10.69 ml it can be concluded that the magnitude of fluoride impurities in the standard acetate solution is not sufficient to influence the results of the potentiometric titration.

Apparatus

All titrations were performed in polyethylene beakers at 25° in a thermostatted room.

The fluoride activity was measured with a fluoride membrane electrode (Orion Research Inc., Model 94-09) using a saturated calomel electrode (Radiometer K 401) as reference. The pH was measured with a glass electrode (Radiometer G 202 B) using the same reference electrode. The potentials of the fluoride and glass electrodes were registered by Radiometer voltmeters (pHM 4 and pHM 22, respectively).

Calibration of the fluoride electrode

In order to test its reproducibility in the presence of acetate, the fluoride electrode was calibrated in different free acetate concentrations. Known amounts of fluoride, acetate and acetic acid were added from a buret to 100 ml of a solution containing a M free acetate and $(1-a)$ M nitrate, the free acetate concentration being kept constant throughout the addition of fluoride. The potential was registered *ca.* 30 min after each addition of titrant. Titrations were performed for six different free acetate concentrations, *i.e.* $a = 0$, 0.1, 0.2, 0.4, 0.6 and 0.8 M, respectively. The results are shown in Fig. 1 in which the measured potential, E mV, has been plotted against the logarithm of the concentration of fluoride added. Since the solutions were buffered at the pK_a value for acetic acid, which is, according to AHRLAND[6], 4.59 in 1 M sodium perchlorate, the ratio of the concentrations of hydrofluoric acid/free fluoride is constant and can be estimated to *ca.* 0.01, using a pK_a value for hydrofluoric acid of 2.58, derived from data due to VANDERBORGH[7]. The amount of HF_2^- is less than 10% of that of HF.

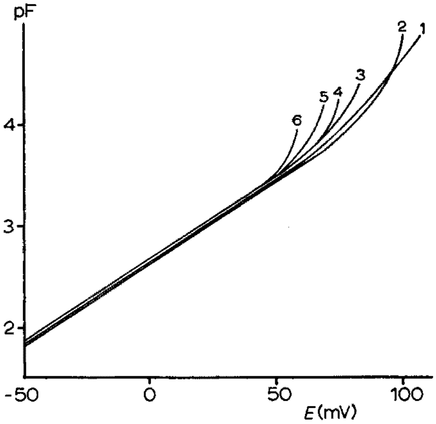


Fig. 1. Calibration curves at 1 M ionic strength for the fluoride electrode. Potential readings have been plotted against the logarithm of the concentration of sodium fluoride added for six different free concentrations of acetate, namely 0, 0.1, 0.2, 0.4, 0.6 and 0.8 M (curves 1–6, respectively).

From the calibration curves in Fig. 1, it is evident that the presence of acetate causes deviation from the Nernst law for pF values greater than 3.6. Since the electrode measures the fluoride concentration at the electrode surface, an increase in the acetate concentration at a given concentration of added fluoride (*e.g.* pF=4) obviously results in a decrease in the electrode potential, E, corresponding to a slow release of fluoride at the electrode surface as the solution is not saturated with respect to lanthanum fluoride. The release of fluoride may either be explained in terms of an ion exchange ($LaF_3(s) + Ac^- \rightleftharpoons LaF_2Ac(s) + F^-$) or in terms of the formation of soluble lanthanum acetate complexes ($LaF_3(s) + nAc^- \rightleftharpoons LaAc_n^{(3-n)} + 3F^-$). It is therefore reasonable to assume that the flow of ions from the electrode surface would be negligible if the solution were already saturated with precipitated lanthanum fluoride and, since this is the case for the titration curves described below, it is perfectly possible that the region of Nernstian behaviour for these curves can be extended beyond pF 3.6.

Titration procedure

Sodium fluoride solution (150 ml of 0.005690 M) was titrated with v ml of 0.03332 M lanthanum nitrate at six different acetate concentrations, the ionic strength being kept constant by means of sodium nitrate. The concentrations of the different species in the buret and in the titration vessel in the six titrations are specified in Table I and the corresponding titration curves are shown as curves 1–6 in Fig. 2. The potential was registered with intervals of at least 30 min, which was the time needed to obtain a constant potential after each addition of titrant. Several sets of data were recorded with the same time interval for each acetate concentration, and the titration curves were found to be fairly reproducible.

TABLE I

TOTAL CONCENTRATIONS IN THE BURET AND IN THE TITRATION VESSEL IN THE SIX TITRATION CURVES SHOWN IN FIG. 2

Titration no.	*Titration vessel*				*Buret*			
	$[F^-]$	$[Ac^-]$	$[HAc]$	$[NO_3^-]$	$[La^{3+}]$	$[Ac^-]$	$[HAc]$	$[NO_3^-]$
1	0.005690	0	0	1.0	0.03332	0	0	0.9
2	0.005690	0.1	0.1	0.9	0.03332	0.1	0.1	0.8
3	0.005690	0.2	0.2	0.8	0.03332	0.2	0.2	0.7
4	0.005690	0.4	0.4	0.6	0.03332	0.4	0.4	0.5
5	0.005690	0.6	0.6	0.4	0.03332	0.6	0.6	0.3
6	0.005690	0.8	0.8	0.2	0.03332	0.8	0.8	0.1

The pH during the titrations

In the titration in the absence of acetate the pH was kept constant by the addition of small amounts of dilute nitric acid or sodium hydroxide. In all measurements in the presence of acetate, it was observed that an increase in the total buffer concentration led to an increase in the measured pH value. This increase, which was of the magnitude of 0.16 pH units when the free acetate concentration was increased from 0.1 M to 0.8 M, may be attributed to the formation of $(HAc)_2$ and HAc_2^-, as proposed by MARTIN AND ROSSOTTI[8], or to changes in the E° value of the glass electrode, as suggested by DANIELSSON AND SUOMINEN[9]. AHRLAND[6], however, observed no increase in pH with increasing total buffer concentration, with the quinhydrone electrode. This was confirmed by DYRSSEN AND HENNICHS[10] who showed that the change in E° could only be detected for the glass and hydrogen electrodes, and that the magnitude of the change was proportional to the concentration of acetate for an ionic strength held constant by means of sodium perchlorate.

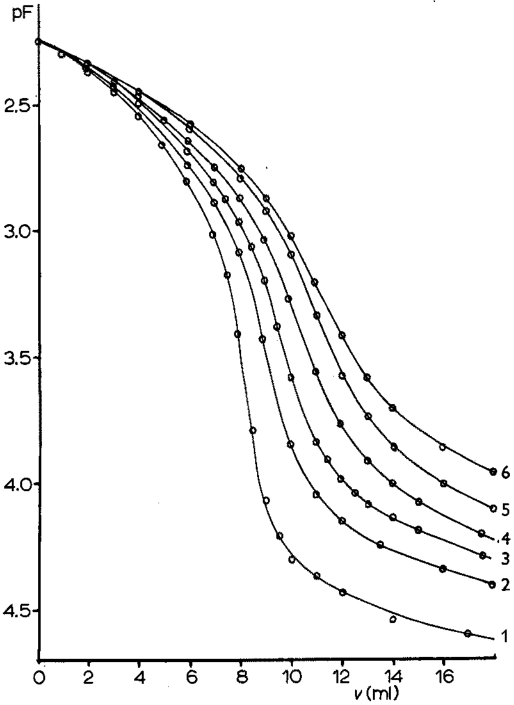


Fig. 2. Titration curves (pF against v ml titrant added) for the titration of 150 ml of 0.005690 M sodium fluoride with v ml of 0.03332 M lanthanum nitrate at six different acetate concentrations 0, 0.1, 0.2, 0.4, 0.6 and 0.8 M (curves 1–6, respectively). The ionic strength is kept constant with sodium nitrate.

RESULTS

The primary titration curves

The titration curves are shown in Fig. 2. It is apparent that the equivalence volumes, evaluated by means of maximum slope of the curve, are greater than the theoretical value, $v_{eq}=8.54$ ml, in all cases where acetate is present and that the discrepancy increases with increasing acetate concentration. This means that the F/La ratio in the solid phase is less than three in the presence of acetate. This may be due to adsorption of lanthanum acetate on the lanthanum fluoride precipitate, as suggested by MEYER AND SCHULZ[11], or to an ion-exchange effect of the type:

$$LaF_3(s) + xAc^- \rightleftharpoons LaF_{3-x}Ac_x(s) + xF^- \qquad (1)$$

Back-titration

Even if the structure of the solid phase is of secondary importance in this investigation, it is vital to study the reversibility of reaction (1) in order to clarify the working of the electrode in acetate medium. Accordingly, 150 ml of a solution containing 0.00570 *M* sodium fluoride, 0.8 *M* sodium acetate and acetic acid were titrated with *v* ml of 0.03332 *M* lanthanum nitrate containing 0.8 *M* sodium acetate and acetic acid. The ionic strength was kept constant at 1 *M* with sodium nitrate (*cf.* curve 6 in Fig. 2). Addition of lanthanum was continued until $F_{tot}-3La_{tot}$ was equal to zero, *i.e.* the theoretical equivalence point corresponding to a total addition of 8.54 ml of lanthanum solution had been reached. The function $(150+v)[F^-]/150$ plotted against excess of fluoride $(F_{tot}-3La_{tot})$ is shown by the solid curve in Fig. 3.

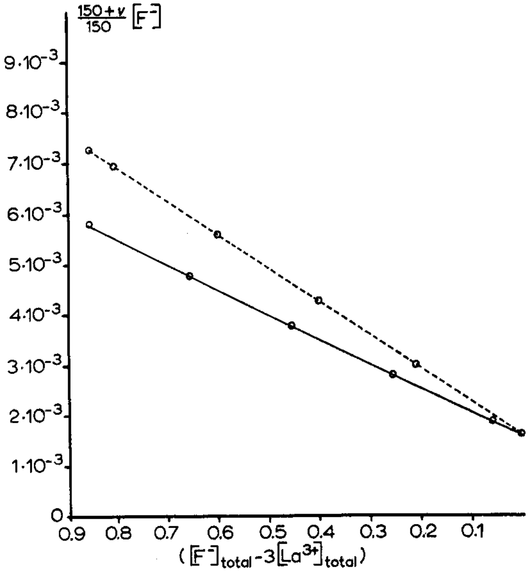


Fig. 3. Titration curve $(150+v)[F^-]/150$ against $F_{tot}-3La_{tot}$ (solid curve), for the titration of 150 ml of 0.00570 *M* sodium fluoride with *v* ml of 0.03332 *M* lanthanum nitrate. Addition of lanthanum was continued until $v = 8.54$ ml where the total amount of fluoride is equal to three times the total amount of lanthanum. The solution was then back-titrated with *v* ml of 0.1005 *M* sodium fluoride (dashed curve: $(158.5+v)[F^-]/150$ plotted against $F_{tot}-3La_{tot}$), until the excess of total fluoride over total lanthanum was the same as it was before the addition of lanthanum nitrate.

The free concentration of fluoride, $[F^-]$, was calculated from the measured *E* values by means of the Nernst equation, and an $E°$ value obtained from the relevant calibration curve in Fig. 1. The solution was then back-titrated with *v* ml of 0.1005 *M* sodium fluoride containing 0.8 *M* sodium acetate and acetic acid until the value of $(F_{tot}-3La_{tot})$ was 0.855 mmol., *i.e.*, the same value as at the commencement of the titration. The resulting titration curve, illustrated by the function $(158.5+v)[F^-]/150$ plotted against $(F_{tot}-3La_{tot})$, is shown by the dashed curve in Fig. 3. Since both titration curves in Fig. 3 are almost linear, it can be concluded that reaction (1) provides a true picture of the equilibria involved only if equilibrium is attained extremely slowly. The linearity of the titration curve for the addition of lanthanum (solid curve in Fig. 3) indicates that the formation of the solid phase can be illustrated schematically as

$$La^{3+}+(3-x)F^-+xAc^- \rightarrow LaF_{3-x}Ac_x(s) \qquad (2)$$

and that the value of x is almost independent of the fluoride concentration in the pF range under consideration. These conclusions are, furthermore, supported by the linearity of the back-titration curve in Fig. 3, which indicates that acetate cannot be removed from the precipitate by the addition of excess of fluoride. A slight exchange may, of course, occur at the crystal surface.

Investigation of the solid phase

In order to investigate the composition of the solid lanthanum fluoride phase precipitated in the presence of acetate, a solution containing 0.05 M sodium fluoride in 1 M acetate was titrated with excess lanthanum nitrate. A reference solid phase was prepared in the same way in the absence of acetate. The two precipitates were centrifuged and washed eight times with doubly distilled water. The washing of the precipitates proved to be difficult, owing to their tendency to colloid formation. After washing, the precipitates were dried at 40° and stored in a desiccator.

The infrared spectra of *ca.* 3-mg portions of the precipitates mixed with 30 mg of potassium bromide, recorded with a Beckman IR 9, are shown in Fig. 4, the dashed curve corresponding to lanthanum fluoride precipitated in the absence of acetate. As may be seen from the interpretation of the spectra in Fig. 4, the existence of carboxylic groups in the solid phase precipitated in the presence of acetate is fully confirmed.

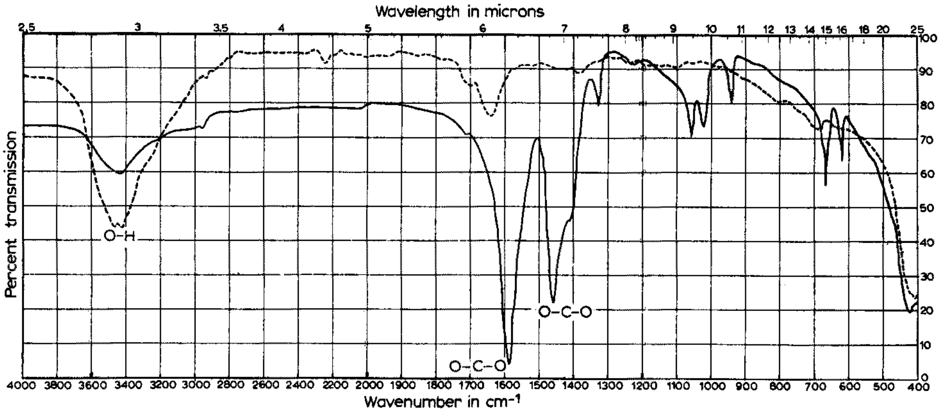


Fig. 4. The IR spectrum of lanthanum fluoride precipitated in the presence (solid curve) and in the absence (dashed curve) of acetate.

In order to determine the amount of acetate in the precipitate quantitatively, the two solid phases were also investigated with a combined differential thermo-analyzer (DTA)–thermobalance (TGA) (Mettler Thermo Analyzer, Serial No. 71). Samples of 30.15 mg of the precipitates were introduced into the thermoanalyzer and heated to 1000°, in a stream of air, at a rate of 8° per min. The results for the two precipitates are shown in Fig. 5 in which the loss in weight has been plotted against the temperature. In both cases a decrease in weight is observed at temperatures between room temperature and 220° due to loss of water adsorbed on the precipitates. In the acetate case there is, moreover, a weight loss commencing at 275° which can be attributed to the decomposition of acetate. This loss was approximately 11.5% of the total weight of the precipitate. Assuming that the decomposition occurs schematically as follows:

$$LaF_{3-x}Ac_x + 2xO_2 \rightarrow \frac{3-x}{3} LaF_3 + \frac{x}{6} La_2O_3 + \frac{3x}{2} H_2O + 2xCO_2 \quad (3)$$

a value of x equal to 0.48 is obtained. This result is in fairly good agreement with the potentiometric titration data. X-Ray investigations of the two precipitates, using the Guiner powder technique with CuKα radiation, indicated that neither of the precipitates was completely crystalline. This made the interpretation of the slight differences observed in the diffraction pattern very difficult.

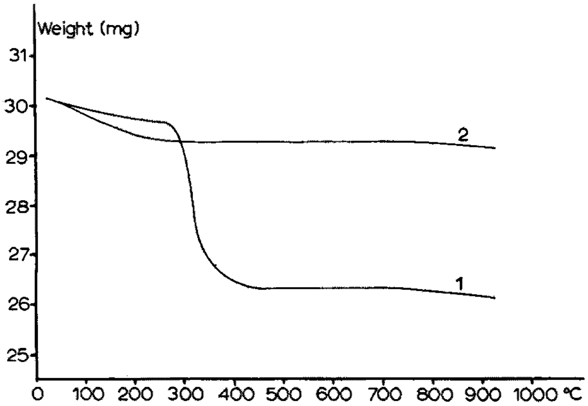


Fig. 5. Thermogravimetric analysis of lanthanum fluoride precipitated in the presence (curve 1) and in the absence (curve 2) of acetate.

EQUILIBRIUM CALCULATIONS ON THE TITRATION CURVES

Calculation of the curve in the absence of acetate

Attempts have been made to calculate the titration curves in Fig. 2 with the HALTAFALL program, assuming that the fluoride electrode obeys the Nernst law and that the system has had time to attain equilibrium. To be able to estimate the effect of different acetate concentrations on the form of the titration curves, it is first necessary to calculate the equilibrium constants in the lanthanum fluoride system at 1 M ionic strength. The experimental data shown in curve 1 of Fig. 2 were used. The form of this titration curve is governed mainly by the solubility product

$$K_{s0} = [La^{3+}][F^-]^3$$

but, for $v > v_{eq}$, the stability constant

$$\beta_1 = [LaF^{2+}]/[La^{3+}][F^-]$$

is also of importance. The lanthanum nitrate complex $LaNO_3^{2+}$, which has a stability constant of the order of magnitude of $10^{-0.26}$ (*cf.* ref. 12), has been neglected in the calculations. At the low fluoride concentrations prevailing for $v > v_{eq}$, the complex LaF_2^+ ($\log \beta_2 = 10^{5.56}$, *cf.* ref. 3) can also be neglected. A value for the solubility product of $pK_{s0} = 17.92$ at $I = 0.01$ M has been determined by LINGANE[2]. The value

$10^{2.70}$ has been suggested for β_1 by IVANOV EMIN *et al.*[13] by analogy with other lanthanide fluoride complexes and we have previously[3] estimated the value of β_1 to be $10^{3.51}$, using data given by LYLE AND NAQVI[14]. With the latter value for β_1 and by varying the value of pK_{s0}, the best fit between experimental and calculated data (v ml against pF) was obtained for a log K_{s0} value of 16.66. The calculated curve is shown as the broken curve 1′ in Fig. 6 and can be compared with the corresponding experimental curve 1. It is evident from Fig. 6 that the value $\beta_1 = 10^{3.51}$ cannot explain the experimental data satisfactorily. Only if the value of β_1 were increased to the very high value of $10^{5.1}$ and the value of log K_{s0} increased to 17.09 would a perfect fit be obtained between experimental and calculated data. The titration curve calculated using these values for the stability constant and the solubility product is shown as the solid curve 1 in Fig. 2.

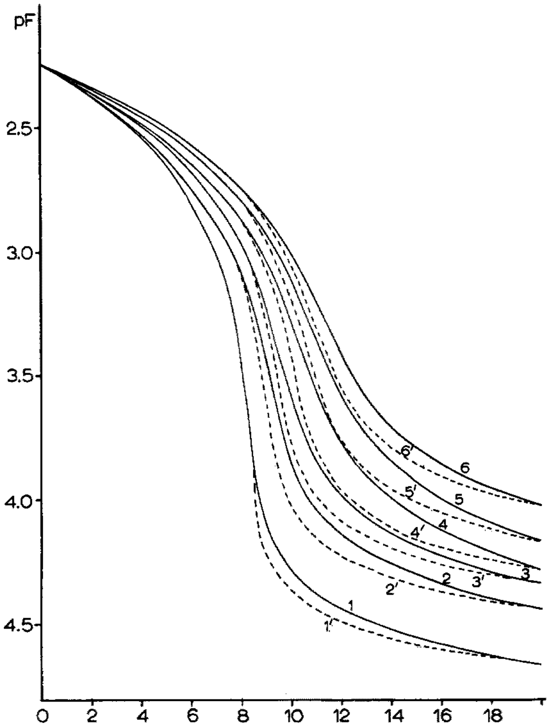


Fig. 6. Titration curves (pF against v ml titrant added) for the titration of 150 ml of 0.005690 M fluoride with v ml of 0.03332 M lanthanum nitrate at six different acetate concentrations 0, 0.1, 0.2, 0.4, 0.6 and 0.8 M (solid curves 1–6, respectively). Calculated titration curves for the same six acetate concentrations using the stability and solubility constants specified in Table II are shown as the dashed curves 1′–6′, respectively.

Calculation of the titration curves in the presence of acetate

The theoretical equivalence volume (assuming formation of LaF_3(s) for all titration curves in Fig. 2) is 8.54 ml. It is, however, obvious (*i.e.* from the location of the inflexion point) that the equivalence volume, v_{eq}, in all titrations performed in acetate medium is appreciably greater than 8.54 ml, due to changes in the solid phase which can be schematically expressed by reaction (2). If, for each titration, the value of x in the volume region $v < v_{eq}$ is constant, x can be determined by a GRAN method. According to reaction (2), the free concentration of fluoride decreases on addition of titrant, *i.e.*

$$[F^-] = 3 \cdot 0.03332\ (v_{eq} - v)/(150 + v);\ v < v_{eq}$$

where v_{eq} is the equivalence volume for reaction (2). Thus, if the GRAN function

$$F_1 = (150 + v)\ 10\ \exp\ \{(E - E_k)F/RT\ \ln 10\} \propto (150 + v)[F^-]$$

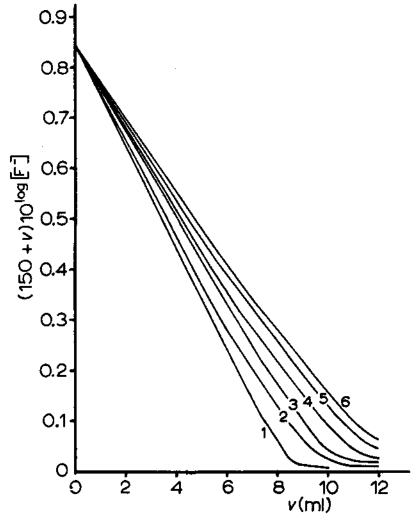
is plotted against v ml of titrant added, a straight line will be obtained if x is constant. The constant E_k can be chosen arbitrarily. The straight line will, moreover, intersect the v-axis at $v = v_{eq}$ when F_1 is extrapolated to zero. From the value obtained for v_{eq}, a value of x can be calculated from the relation:

$$150 \cdot 0.005690 = (3 - x)\ v_{eq} \cdot 0.03332$$

GRAN plots, $F_1 = (150 + v)$ 10 exp log $[F^-]$, calculated from experimental data for the six titration curves 1–6 in Fig. 2 are shown as the straight lines 1–6 in Fig. 7. The values of x obtained for different acetate concentrations are specified in Table II and the dependence of x on the free acetate concentration is illustrated in Fig. 8.

In the HALTAFALL calculations of the curves obtained in the presence of acetate, a solubility product

$$K_{s0} = [La^{3+}][F^-]^{3-x}[Ac^-]^x$$



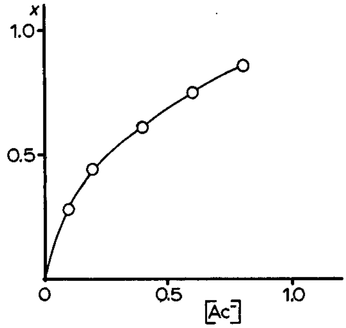


Fig. 7. GRAN plots, $(150 + v)$ 10 exp. log $[F^-]$ against v ml of titrant added, for the titration of 150 ml of 0.005690 M fluoride with v ml of 0.03332 M lanthanum nitrate at six different acetate concentrations, 0, 0.1, 0.2, 0.4, 0.6 and 0.8 M (curves 1–6, respectively).

Fig. 8. The dependence of the value of x on the free acetate concentration when a solution containing fluoride and acetate is titrated with lanthanum and a precipitate with the composition $LaF_{3-x}Ac_x$ is formed.

TABLE II

FEASIBLE VALUES FOR THE STABILITY AND SOLUBILITY CONSTANTS IN THE La^{3+}–F^-–Ac^- SYSTEM USED TO CALCULATE THE TITRATION CURVES 1′–6′ OF FIG. 5

Curve no. in Fig. 5	$[Ac^-]$	X	$\log K_{s0}$	$\log \beta_{LaF}$	$\log \beta_{LaFAc}$
1′	0	0	−16.66	3.51	—
2′	0.1	0.27	−16.03	3.51	4.32
3′	0.2	0.44	−15.61	3.51	4.32
4′	0.4	0.61	−15.40	3.51	4.32
5′	0.6	0.75	−14.97	3.51	4.32
6′	0.8	0.86	−14.54	3.51	4.32

was introduced, using the value of x obtained by the GRAN method. The following lanthanum–acetate complexes have been taken from SONESSON[15].

$La^{3+} + Ac^- \rightleftharpoons LaAc^{2+}$ $\log \beta_1 = 1.56$

$La^{3+} + 2Ac^- \rightleftharpoons LaAc_2^+$ $\log \beta_2 = 2.48$

$La^{3+} + 3Ac^- \rightleftharpoons LaAc_3$ $\log \beta_3 = 2.98$

$La^{3+} + 4Ac^- \rightleftharpoons LaAc_4^-$ $\log \beta_4 \sim 2.95$

The computer calculations were first performed for the five different acetate concentrations using feasible values for the stability constants of LaF^{2+} and LaF_2^+ selected from the literature[3], *i.e.* $10^{3.51}$ and $10^{5.56}$, respectively. Since previous work indicated the possibility of mixed lanthanum–fluoride–acetate complexes, one such complex, $LaFAc^+$, was introduced into the calculations and its stability constant was estimated to be

$$\beta_{LaFAc^+} = 2(\beta_{LaF_2^+} + \beta_{LaAc_2^+})^{\frac{1}{2}} = 10^{4.32}$$

using a method described by DYRSSEN *et al.*[16].

By means of the above values for the stability constants, the value of K_{s0} was varied until the best fit was obtained between calculated and experimental curves. The calculated curves are shown by the broken curves 2′–6′ in Fig. 6 and may be compared with their corresponding experimental curves, 2–6, respectively. The stability constants and solubility products used to calculate the curves 1′–6′ of Fig. 6

TABLE III

STABILITY AND SOLUBILITY CONSTANTS IN THE La^{3+}–F^-–Ac^- SYSTEM CALCULATED FROM THE EXPERIMENTAL CURVES

Curve no. in Fig. 5	$[Ac^-]$	X	$\log K_{s0}$	$\log \beta_{LaFAc}$
1	0	0	−17.09	—
2	0.1	0.27	−16.65	6.10
3	0.2	0.44	−16.20	6.50
4	0.4	0.61	−16.43	7.70
5	0.6	0.75	−15.43	7.35
6	0.8	0.86	−14.69	7.00

are specified in Table II. From Fig. 6 it is seen that the set of data given in Table II cannot satisfactorily explain the form of the experimental curves. The values of K_{s0} and β_{LaFAc^+} were therefore varied until a good fit between experimental and calculated data was obtained. The different values of K_{s0} and β_{LaFAc^+} corresponding to the five different acetate concentrations are listed in Table III. It is seen from the table that it would be necessary to increase the value of β_{LaFAc^+} drastically if the experimental curves were to be explained by the law of mass action.

DISCUSSION

The solid phase has been shown to contain acetate, and, since the amount of acetate in the precipitate is appreciable, it is hard to believe that surface adsorption alone could account for this phenomenon. The crystal structure of lanthanum trifluoride consists of parallel LaF^{2+} layers with the remaining F^- ions situated between the layers and is similar to the structures of many LaO^+ and BiO^+ compounds. It has been shown that it is possible to introduce small amounts of anions of non-branched carboxylic acids into crystals of BiOCl[17] and it is reasonable to suppose that a similar phenomenon might occur for lanthanum trifluoride precipitated in the presence of acetate, and even for the lanthanum trifluoride crystal of the membrane electrode. Such an ion exchange at the surface of the crystal will continuously shift the $E°$-value and cause the electrode to work sluggishly. This has been observed, and it was, moreover, possible to repair the electrode by polishing the surface of the crystal with diamond paste (0.25–0.5 μm in diameter).

In this investigation, titrations were done slowly in order to attain equilibrium; rapid titrations would, of course, result in the introduction of smaller amounts of acetate into the precipitate. It is our intention to investigate the behaviour of the fluoride membrane electrode in media containing other ions which may be likely to replace fluoride in the lanthanum trifluoride crystal.

The methyl group of the acetate ion appears to hinder the exchange between fluoride ions in the crystal and in the bulk of the solution by blocking the crystal surface. The electrode thus registers too high a fluoride concentration after the equivalence point. In calculations based on a Nernstian behaviour, this effect would result in too high values for, for instance, the stability constant of $LaFAc^+$, which might explain the unbelievably high values given in Table III. High concentrations of nitrate ions might have a similar effect on the electrode, which would explain the apparent increase in the stability of the complex LaF^{2+} seen in Table II.

If, on the other hand, the electrode obeyed the Nernst law throughout the concentration range of the titrations, the most probable explanation of the value of the stability constant for $LaFAc^+$ is a sudden increase in the acetate content of $LaF_{3-x}Ac_x$ in the volume region immediately after the equivalence point. Since, however, ion exchange has been shown to occur only very slowly at the higher concentrations of fluoride before the equivalence volume, there are reasons to believe that it will do so even after the equivalence point. Irrespective of which model is the correct one, it can be concluded that carboxylic acid buffers are unsuitable for all work involving the lanthanum fluoride electrode.

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SUMMARY

Precipitation titrations of fluoride with lanthanum nitrate using a lanthanum fluoride electrode have been carried out at constant ionic strength and different acetate concentrations. The titration curves have been analysed by rigorous equilibrium calculations with the computer program HALTAFALL. Acetate ions have been shown to enter the solid phase, forming precipitates with the formula $LaF_{3-x}Ac_x$ ($0 < x < 1$). The presence of acetate causes the electrode to work sluggishly and to deviate from the Nernst law. These effects increase with increasing acetate concentrations and may possibly even occur at high nitrate concentrations.

RÉSUMÉ

On décrit un titrage des fluorures par précipitation au moyen de nitrate de lanthane, en utilisant une électrode à fluorure de lanthane. Ce titrage se fait à force ionique constante et à différentes concentrations en acétate. Les courbes de titrage ont été analysées par calculs d'équilibre rigoureux à l'aide du computer HALTAFALL. On observe que les ions acétates entrent dans la phase solide, formant des précipités.

ZUSAMMENFASSUNG

Es wird die Fällungstitration von Fluorid mit Lanthannitrat unter Verwendung einer Lanthanfluorid-Elektrode und bei konstanter Ionenstärke und verschiedenen Acetatkonzentrationen beschrieben. Die Titrationskurven wurden mit dem HALTAFALL-Rechenprogramm analysiert. Es zeigte sich, dass Acetationen unter Bildung von Niederschlägen in die feste Phase übergehen.

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DETERMINATION OF VALENCE STATES OF IRON IN GLASS AND OF URANIUM IN CALCIUM FLUORIDE SINGLE CRYSTALS

U. ABED
Lawrence Radiation Laboratory, University of California, Berkeley, Calif. 94720 (U.S.A.)
(Received May 26th, 1969)

During studies in this laboratory, it became necessary to determine the iron(II) and iron(III) oxide content of sodium disilicate glasses which had been used in high-temperature electrochemistry experiments. A wealth of publications deals with the determination of iron(II). Among others, CHENG[1] discusses various methods for the determination of iron(II) oxide in some solids and, stating the limitations for his purpose, developed a procedure for determining iron(II) in ferrites. However, his approach is unsuitable for the decomposition of glass. A method described by CLOSE *et al.*[2] for iron(II) in glass was selected. They recommend a hydrofluoric–sulfuric acid mixture for the dissolution of glass under an inert atmosphere, followed by titration of the liberated iron(II) with cerium(IV). The iron(II) results obtained by this procedure in this laboratory were widely scattered, and attempts to modify the method did not improve the precision.

The method presented here is based on the fact that cerium(IV) is stable for an extended period over the temperature range 20–100° in the hydrofluoric–sulfuric acid mixture. This permits the instantaneous oxidation of the released iron(II) by a known excess of standard cerium(IV) solution during the dissolution of the glass and thus obviates the need for an inert atmosphere. The results obtained on glass samples by this procedure are precise and the accuracy of the determination on simulated samples was within 1%. The method is also applicable to the determination of iron(II) oxide in magnesium oxide. The formal oxidation potentials for the cerium(IV)–cerium(III) couple and for the iron(III)–iron(II) couple are estimated in the glass-dissolving acid mixture and their importance is discussed. The procedure was further employed in determining valence states of semi-micro quantities of uranium in calcium fluoride single crystals.

EXPERIMENTAL

Apparatus

Teflon beakers with pouring lips, 3.4 cm o.d., 2.7 cm i.d., and 4.6 cm high, with a capacity of 30 ml, were machined from commercial rod stock and were fitted with Teflon covers. Teflon-covered magnetic stirring bars, in conjunction with Mag-Mix magnetic stirrers, were used to agitate the glass–acid mixtures. Micro washout pipets, guaranteed "to contain" within ±0.01% of the stated volume, were used to aliquot the standard solutions and the indicator. Hydrofluoric acid was aliquoted with 2.0-ml plastic pipets. A previously described lead column reductor was used in determining the total uranium[3] and the total iron[4]. The potential measurements were made with a Digi-Tec digital d.c. voltmeter.

Reagents

All chemicals used were reagent grade unless otherwise specified. Sufficient cerium(IV) ammonium nitrate was dissolved in sulfuric acid to give, on final dilution, a stock solution 0.1 *M* in cerium(IV) and 1 *M* in sulfuric acid; 0.01 *M* cerium(IV) solutions were prepared by dilution of the stock solution while maintaining a sulfuric acid concentration of 10% by volume. The 0.1 *M* solution was stable for at least 2 years, and the 0.01 *M* dilution was stable for at least 3 weeks. A standard 0.001 *M* iron(II) ammonium sulfate solution, 10% by volume in sulfuric acid, was prepared daily by direct weighing. Sufficient iron wire for standardization was dissolved with hydrochloric acid to give a solution of 0.1 *M* iron(III) on dilution. A 1:20 dilution of the commercially available 1,10-phenanthroline iron(II) sulfate (ferroin) indicator, 0.025 *M*, from G. F. Smith Chemical Company was employed. Concentrated sulfuric acid and 48% hydrofluoric acid were purified with permanganate as described previously[2] and were used throughout the procedure for iron. N.B.S. uranium dioxide, 0.1 *M* iron(III) sulfate solution, and a calcium fluoride single crystal were used in the uranium determination.

Potential measurements

The formal oxidation potential measurements of the cerium(IV)–cerium(III) couple were conducted in a 100-ml polyethylene cell, with a platinum wire and a Lingane-type saturated calomel electrode (SCE) combination. Diffusion of the potassium chloride into the cell and contact of the glass electrode with hydrofluoric acid is not desirable, therefore the electrical contact through the cell was accomplished by allowing the SCE bridge to dip into a 5 *M* ammonium nitrate solution, and by bridging from there into the cell by a bees' wax-coated U-tube with an upturned tip. The agar-agar salt bridge was avoided because strong oxidants are known to attack it[5]. The entire cell and associated parts were immersed in a 25.0° ± 0.1° constant temperature bath.

The solution used consisted of 1.00 ml of 0.0992 *M* cerium(IV) and 1.00 ml of 0.0992 *M* cerium(III), both in 1 *M* sulfuric acid, 10 ml of hydrofluoric acid, 10 ml of sulfuric acid, and 20 ml of water. The mixture was stirred continuously with a magnetic stirrer while potential measurements were made at 5-min intervals.

The measurement of the iron(III)–iron(II) formal oxidation potential was made in the same cell as described above. In this case the bridge solution was saturated potassium sulfate, since contact of an iron(II) solution with a strong nitrate solution might result in oxidation of the iron(II). The iron(III)–iron(II) potential was measured on a solution similar to the one above, but containing 1.00 ml of 0.0988 *M* iron(III) and 1.00 ml of 0.0999 *M* iron(II) instead of cerium. Before aliquoting the iron into the acid–water solution, the mixture was purged of oxygen with a chip of Dry Ice. Carbon dioxide gas was directed over the surface of the solution during the time the potential measurements were made.

Standardization of 0.01 M ceric sulfate

Deliver a 3-ml aliquot of the 0.1 *M* standard iron solution into a 30-ml platinum crucible and fume almost to dryness with 1 ml of sulfuric acid and 2 ml of hydrofluoric acid. Transfer the sample to a 50-ml beaker, add 5 ml of 4 *M* hydrochloric acid, and dilute to 25 ml. Wash the iron through a lead column reductor with six 25-ml portions of 0.8 *M* hydrochloric acid. Receive the eluent in a 500-ml Erlenmeyer flask which contains 10 g of boric acid and sufficient Dry Ice to provide an inert atmosphere throughout the subsequent titration. Aliquot 4 ml of sulfuric acid and 1 ml of 1:20 ferroin solution into the sample flask. While stirring, titrate with the 0.01 *M* cerium(IV) solution to the end-point. Determine indicator and reagent blanks and apply the appropriate titer corrections to the results.

Determination of iron(II)

Grind a glass sample in a Diamonite mortar to pass 100 mesh. Weigh 100 mg of the glass to give 0.4–1.0 mg of iron(II) oxide. Transfer the sample to a Teflon beaker and aliquot 2 ml of 0.01 *M* standard cerium(IV) solution, 2 ml of hydrofluoric acid, and 1 ml of sulfuric acid into the beaker. Stir the mixture magnetically until the glass has dissolved. Some samples require hot acids to effect dissolution. They may be heated for 24 h or more in a water bath at 100° without destroying the oxidant. Blanks are treated similarly. Add 10 g of boric acid to the dissolved sample and stir for an additional 5 min. Transfer the sample solution to a 250-ml Erlenmeyer flask and aliquot 4 ml of sulfuric acid and 1 ml of 1:20 ferroin solution into the sample container. Dilute to 100 ml and, while stirring, titrate with standard 0.001 *M* iron(II) ammonium sulfate to the end-point. Up to 10 mg of iron(II) oxide can be determined by employing the standard cerium(IV) stock solution and a standard 0.01 *M* iron(II) ammonium sulfate titrant.

Determination of total iron

Weigh 50–100 mg of the 100-mesh glass sample to give 0.5–1.0 mg of Fe_2O_3. Transfer the sample to a 30-ml platinum crucible and treat the glass as described above for the standardization of the cerate solution. When the sample has dissolved, proceed with the column reduction. Receive the eluent in a 500-ml Erlenmeyer flask which contains a 2-ml aliquot of the 0.01 *M* standard cerium(IV) solution and 10 g of boric acid. Magnetically stir the cerium(IV)–boric acid mixture while receiving the eluent. Add 4 ml of sulfuric acid and 1 ml of 1:20 ferroin solution. Titrate the excess of standard cerium(IV) with standard 0.001 *M* iron(II) ammonium sulfate to the end-point. Up to 10 mg of total iron can be determined by employing the standard cerium(IV) stock solution and a standard 0.01 *M* iron(II) ammonium sulfate titrant.

Valence determination of uranium

Grind a calcium fluoride–uranium sample in an agate mortar to pass 100 mesh. Weigh 100–200 mg to give 0.1–1.0 mg of uranium. Weigh 100–200 mg of a finely ground calcium fluoride single crystal, which serves as part of the blank. Transfer the samples to 250-ml Erlenmeyer flasks and aliquot into each 3 ml of 0.01 *M* standard cerium(IV) sulfate solution, 1 ml of iron(III) sulfate solution and, after the addition of 2.5 g of boric acid, 1 ml of perchloric acid. Suspend the flasks in a boiling water bath and stir the solutions magnetically. When the samples have dissolved, dilute them to 150 ml with distilled water, adding 5 ml of sulfuric acid and one drop of

0.025 M ferroin indicator. Titrate the excess of cerium(IV) with standard 0.001 M iron(II) ammonium sulfate.

An independent determination for total uranium must be made on another portion of the sample in order to calculate the change in valence.

DISCUSSION

Iron(II) and (III)

The instantaneous oxidation of iron(II) released upon dissolution of a glass sample has obvious benefits. However, the strong oxidant selected must be stable with respect to light, time, and temperature, and must be compatible with the highly acidic glass-dissolving mixture. Dichromate and permanganate proved useless. On the other hand, sulfatocerate, in molar sulfuric acid, is stable to light; it has an excellent, long-term stability, and it can be boiled for several hours without significant decomposition[6,7]. Also, data obtained in this laboratory indicate that it is stable in the hydrofluoric–sulfuric acid mixture, employed in the recommended procedure, for at least six days at room temperature and for more than 24 h at 100°.

When sulfatocerate is added to a solution containing hydrofluoric acid, the familiar yellow disappears. Fluoride complexes cerium(IV) and probably decreases the oxidation potential of the system. It was thought, therefore, to be of value to estimate the formal oxidation potential. A range of values from 0.7 V to 0.9 V was obtained for the oxidation potential of the cerium(IV)–cerium(III) couple at 25°. Several problems were attendant: the cerium(III) fluoride gradually forms a gelatinous precipitate which coats the platinum wire, resulting in varying potential readings. The potential obtained is not strictly a "formal oxidation potential" since both the oxidized and the reduced forms do not remain in solution. However, the potential obtained is sufficiently positive to oxidize iron(II) under the same conditions. Addition of 10 g of boric acid results in dissolution of the cerium(III) fluoride and in a marked increase in potential, up to a stable 1.31 V, due to release of cerium(IV) ion by borate–fluoride complexing. Further addition of boric acid does not affect the readings. The value reported here is lower than the commonly stated value of 1.44 V and may indicate some residual cerium(IV)–fluoride complexing, although the solution measured is saturated with boric acid. The values presented are not corrected for the junction potential.

The strong fluoride complexing of iron(III), but not that of the iron(II), is well known. Therefore, the low formal oxidation potential of 0.51 V obtained under the recommended conditions was expected. When the fluoride was masked with boric acid, a potential of 0.62 V was obtained. Since iron(III) is complexed by sulfate ($\log \beta_2 = 5.2$), the value reported here, although lower than that obtained in 1 M sulfuric acid (0.68 V), is acceptable. The oxidation potential of oxygen (1.229 V) is considerably more positive than the values reported for the iron(III)–iron(II) couple in either fluoride or sulfate media and, therefore, oxygen must be excluded.

A study was made to correlate the particle size of a commercial glass with the time required for dissolution, and to determine whether there was any relationship between the particle size and the iron(II) content found. The glass was ground in a Diamonite mortar and sieved to give >20 mesh, <20 mesh, <48 mesh, <80 mesh, and <100 mesh. Approximately 100 mg of each mesh size was dissolved in duplicate for 150 min in the hydrofluoric–sulfuric acid and cerium(IV) mixture to establish the amount of iron(II) present. The dissolution time was then shortened with decreasing particle size. Triplicate and quadruplicate results were secured in most cases. The minimum time required for dissolving the particular glass at hand was: <100 mesh, 10 min; <80 mesh, 20 min; <48 mesh, 45 min; <20 mesh, 100 min; >20 mesh, 120 min. The iron(II) content was independent of the length of time of grinding. Evidently, no oxidation of iron(II) occurred during prolonged grinding (5 days) or during exposure to air of the finely ground sample, supporting the views of HILLEBRAND[8] and DENSEM[9]. The average value of 35 completely dissolved samples was 0.374% iron(II), covering the range from 0.355% to 0.391%, with a standard deviation of 0.01%. The basis upon which dissolution was judged to be complete were the values obtained for all mesh sizes after 150 min of dissolving. Based on the foregoing findings, sodium disilicate glasses, which had been used in high-temperature electrochemistry experiments, were analyzed according to the recommended procedure. Reproducible results are represented by: Sample A, 19.12±0.5% iron(II) (5 determinations) and, Sample B, 25.90±0.15% iron(II) (3 determinations).

A potentiometric determination of micro amounts of iron(II) described in the literature[10] seemed to have several drawbacks; in particular, that the glasses submitted for analysis could not be dissolved within 5 min as could those cited. The present method was therefore tested on the semi-micro scale. Standard glasses are not available and had to be simulated by using iron-free quartz wool and known quantities of standard iron(II) ammonium sulfate. The amount of iron(II) found was within 1% of the amount added (Table I). Table II illustrates the precision obtained

TABLE I

SEMI-MICRO ANALYSIS OF IRON(II) AMMONIUM SULFATE AND QUARTZ WOOL

mmoles Fe(II)		*% Error*
Added	*Found*	
0.01003	0.00990	−1.3
0.01003	0.00995	−0.8
0.01003	0.00995	−0.8
0.00501	0.00499	−0.4
0.00501	0.00504	+0.6

TABLE II

ANALYSIS OF INDUSTRIAL GLASSES

Sample	*Quoted*	*Found*	*No. of detns.*	*Std. dev. (%)*	*Range (%)*
Fe(II) (%)					
1	0.281	0.306	8	±0.002	0.302–0.309
2	0.546	0.573	9	±0.008	0.560–0.587
3	0.350	1.19	8	±0.003	1.17–1.26
Total iron (%)					
1	0.322	0.424	5	±0.011	0.413–0.442
2	0.588	0.660	4	±0.020	0.635–0.685
3	1.19	1.42	4	±0.060	1.36–1.48

for analysis of industrial glasses containing 1% or less of iron(II). The analytical data quoted by the manufacturer for iron(II) and for total iron were usually lower than the results obtained with the proposed method.

For the determination of total iron, an inert atmosphere was eliminated by receiving the reduced eluent in an excess of standard cerium(IV), which was back-titrated with standard iron(II) ammonium sulfate. The titration end-point could be observed more carefully without the Dry Ice, splashing of the sample solution was avoided, and the solutions did not have to be titrated immediately. The accuracy obtained with a series of simulated samples was within 0.3% of the amount of total iron present.

Furthermore, ratios of iron(II) to iron(III) were determined in magnesium oxide crystals which were used in electron paramagnetic resonance studies. The ratios obtained by the recommended procedure, but omitting hydrofluoric and boric acid, were in good agreement with the theoretical values.

The method applies to glasses and to materials which do not contain reducing substances other than iron(II) and which can be dissolved at 100° or less. It should be feasible to determine micro amounts of iron(II) by a slight modification of the proposed method in which the final titration with iron(II) ammonium sulfate is substituted by a spectrophotometric determination of the excess of cerium(IV) at 350 nm.

The suggested procedure has the following advantages over existing methods for the FeO determination in glass: (1) better precision, (2) elimination of an inert atmosphere for the iron(II) as well as for the total iron determination, (3) stability of the oxidant at 100°, and (4) simplicity of operation with common, inexpensive laboratory equipment. Many samples may be determined simultaneously during a working day.

Uranium

The principle of an instantaneous oxidation was applied to the determination of the oxidation state of uranium in calcium fluoride single crystals, the properties of which are being studied by optical spectroscopy. These crystals contained 0.1–0.8% of uranium believed to be in the +3 or the +4 oxidation state. An iron(III) catalyst was required to hasten the oxidation of uranium(IV) to uranium(VI) by cerium(IV).

Preliminary tests were made with simulated samples, using N.B.S. uranium dioxide and reagent-grade calcium fluoride. The reagent blank for 100 mg of calcium fluoride, combined with the acids and the indicator used in the recommended procedure, consumed 40% of the added standard cerium(IV). In view of a desired overall accuracy of ±10% in the valence determination, a 40% blank could not be tolerated. Instead, a finely ground calcium fluoride single crystal was used in subsequent work. This crystal was grown from specially purified reagents for optical studies. The value of the blank decreased to 10% of the added standard cerium(IV). It was proved that this blank was not due to the calcium fluoride, but exclusively to the acids and indicator.

It has been stated[11] that calcium fluoride can be readily dissolved in hot hydrochloric acid in the presence of fluoride-complexing cations. An investigation showed that hydrochloric acid was not an efficient solvent, and that cerium(IV) apparently oxidized chloride to chlorine. Perchloric acid was chosen for the recommended procedure because it dissolved the calcium fluoride crystals within several hours just below 100° and did not interfere with the oxidant.

Accuracy

The method was applied to simulated samples consisting of a calcium fluoride single crystal to which known quantities of N.B.S. uranium dioxide were added. Approximately 100 mg of calcium fluoride were combined with approximately 2.5 mg of uranium dioxide. The results obtained by titrating the excess of cerium(IV) were low by an average of 10%. A lead column reduction of known mixtures of uranium dioxide (2.5 mg) and calcium fluoride (100 mg) in perchloric acid, oxidized first to the +6 valence state with hydrogen peroxide, gave a 4% positive error for the determination of total uranium.

A pink single crystal, consisting of calcium fluoride and uranium in the +3 oxidation state as evidenced by the characteristic color, was analyzed in quadruplicate. The precision was ±0.13%. Not enough material was available to permit the determination of total uranium and therefore, the initial valence could not be confirmed.

A green single crystal, however, was analyzed for total uranium by two independent methods. Neutron activation analysis in duplicate gave 0.79% and 0.82% uranium. A spectrophotometric determination in duplicate[12] resulted in 0.81% and 0.80% uranium. The determination of the change in oxidation state of the uranium by cerium(IV) titration to uranium(VI) gave a value of 2.06 (±5%), indicating the presence of uranium(IV) in the crystal (Table III).

Obviously, the method cannot be used without modification if mixtures of several valences and/or reducing substances are present. Additional investigations of the various oxidation states of uranium in calcium fluoride and in other solid materials are in progress.

TABLE III

SEMI-MICRO DETERMINATION OF URANIUM IN CALCIUM FLUORIDE

meq·10⁻⁵ found	*mmoles·10⁻⁵ U found*	*Oxidation change*
6.57	3.32[a]	1.94
6.88	3.44[a]	2.04
6.92	3.36[b]	2.05
7.18	3.40[b]	2.12
7.31		2.16
	av. 3.38	av. 2.06

[a] Neutron activation analysis.
[b] Spectrophotometry.

SUMMARY

The instantaneous oxidation of macro and semi-micro amounts of iron(II) in various types of glasses, of iron(II) in magnesium oxide, and of semi-micro quantities of uranium(III) or uranium(IV) in calcium fluoride single crystals, by excess of cerium(IV) present in the solvent system, followed by back-titration with iron(II)

ammonium sulfate, is the basis for a simple, accurate method which, furthermore, obviates the need for an inert atmosphere. Formal oxidation potentials of the Ce(IV)/Ce(III) couple and the Fe(III)/Fe(II) couple in the hydrofluoric–sulfuric acid glass-dissolving mixture were estimated.

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FLUORIMETRIC DETERMINATION OF OXIDATIVE ENZYMES

ANALYTICAL APPLICATIONS OF THE MONOAMINE AND DIAMINE OXIDASE SYSTEMS

G. G. GUILBAULT, S. S. KUAN AND P. J. BRIGNAC, JR.
Department of Chemistry, Louisiana State University in New Orleans, Lakefront Campus, New Orleans, La. 70122 (U.S.A.)

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The oxidation of amines by the enzymes diamine and monoamine oxidase proceeds via the following reaction:

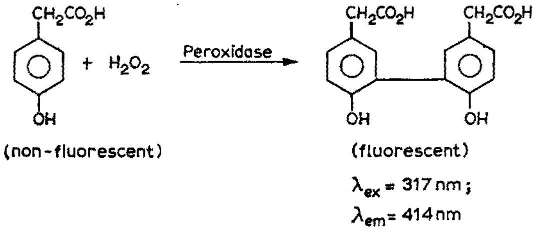
$$RCH_2NH_2 + O_2 + H_2O \rightleftharpoons RCHO + NH_3 + H_2O_2$$

The rate of this reaction has been followed by measuring all of the products and reactants. A good review of some of this work has been published[1]. *o*-Dianisidine has been used with peroxidase to follow the evolution of hydrogen peroxide[2] and radiometric methods have also been developed[3-5]. These methods have increased the sensitivity of detection of the enzymes.

GUILBAULT *et al.*[6,7] have described the use of homovanillic acid (HVA), 3-methoxy-4-hydroxyphenylacetic acid, for the quantitative determination of oxidative enzymes. Hydrogen peroxide formed in the oxidase reactions can be measured by coupling it to the formation of a fluorophore with HVA in the presence of peroxidase. GUILBAULT *et al.*[8] showed that *p*-hydroxyphenylacetic acid could be used in place of HVA. This substrate had advantages over HVA of low cost and a higher fluorescent coefficient.

Recently, SNYDER AND HENDLEY[9] described the use of HVA to develop a simple and sensitive fluorescent assay for monoamine oxidase and diamine oxidase. The method is comparable in sensitivity to radiometric techniques, and is based on a total fluorescent reading after subtracting the blank. The assay requires a one-hour incubation at 37° with continuous shaking.

To avoid the incubation time, the authors developed a very simple and rapid assay for these enzymes and some of their substrates. Instead of HVA, the better substrate *p*-hydroxyphenylacetic acid was employed in an initial rate method:



The assay can be performed in less than 3 min by measuring the initial rate of production of the fluorophore and comparing this rate to a calibration plot of rate *vs.* concentration.

Analytical methods were developed for diamine oxidase (hog kidney), monoamine oxidase (beef blood), and the amines: cadaverine, histamine, putrescine, benzylamine, tyramine, and furfurylamine. In all of the analyses, the error was less than about 3%.

EXPERIMENTAL

All solutions were prepared using triply distilled water. Once-distilled water was doubly distilled, from first alkaline then neutral potassium permanganate.

Enzymes

Peroxidase. An aqueous 1 mg/ml solution of horse radish peroxidase (B grade, RZ=0.3, Calbiochem. Co., activity from assay[10] was 125 units/mg) was prepared.

Monoamine oxidase. A highly purified monoamine oxidase was prepared from beef blood by the method of YAMADA AND YASUNOBU[11], with the omission of crystallization and the modification of step 3, in which Sephadex G-100 chromatography was used instead of DEAE-cellulose chromatography. The preparation of gel and the packing of the column were performed as described in the Pharmacia Sephadex manual[12]. After the column had been equilibrated with 0.003 M phosphate buffer (pH 7.0), the sample was applied. The column was then eluted with 0.005 M phosphate buffer at pH 7.0. The active fractions were collected, combined, and concentrated to about one-twentieth of its original volume by freeze-drying. The concentrated enzyme solution was dialyzed overnight against 100 volumes of 0.003 M phosphate buffer (pH 7.0). This dialyzed enzyme solution was subjected to DEAE-cellulose chromatography. The active portions were combined and a standard spectrophotometric assay was run[13]. From this assay the activity of monoamine oxidase was calculated to be 99.0 units/ml; a unit represents the amount of monoamine oxidase catalyzing an increase in absorbance of 0.001/min at 250 nm.

A very active diamine oxidase was prepared from hog kidney by a modification of the method of MONDOVI *et al.*[14]. The general procedure and conditions for the purification of this enzyme were the same as described by these authors, except that Sephadex G-100 column chromatography was used instead of column electrophoresis. The preparation and elution of the column, and the concentration of the enzyme solution were the same as described for monoamine oxidase. Diamine oxidase activity was determined spectrophotometrically by a method based on the coupling reaction of Δ'-pyrroline type compounds with *o*-aminobenzaldehyde[15]. The incubation mixture contained 3.5 ml of 0.1 M phosphate buffer, pH 9.5, 0.5 ml of 0.025 M *o*-aminobenzaldehyde, 0.2 ml of catalase solution (20 μg), 0.5 ml of 0.06 M putrescine, and 0.3 ml of diluted diamine oxidase. The reaction was stopped after 10 min by the addition of 1 ml of 15% trichloroacetic acid. Absorbances were measured against the blank at a wavelength of 430 nm. One unit of diamine oxidase is defined as the amount of enzyme that will catalyze the transformation of 1 μmole of putrescine at 37°. The molar extinction coefficient used was reported previously[16], and was 2370 l mole^{-1} cm^{-1} at 430 nm. The diamine oxidase activity was found to be 70 units/ml.

o-Aminobenzaldehyde used in the assay was prepared by a procedure listed in *Organic Synthesis*[17].

Buffers

Tris(hydroxymethyl)aminomethane buffer (0.1 *M*) was prepared by dissolving the pure compound (Sigma) in triply distilled water and adjusting the pH with concentrated hydrochloric acid. The pH used for analysis depended upon the particular substrate.

Substrates

A 3.7 mg/ml solution of *p*-hydroxyphenylacetic acid (Columbia Organic) was prepared in water. The substrates, cadaverine dihydrochloride, histamine dihydrochloride, and tyramine hydrochloride were obtained from Sigma (St. Louis). Putrescine, benzylamine (Eastman, Rochester) and furfurylamine (K + K Laboratories) were distilled before use.

Apparatus

Fluorescent measurements were made with an Aminco-Fluoromicrophotometer filter instrument. The lamp used was a Turner 110-850 general-purpose UV lamp. The excitation filter used was a Corning 7-60 (4.5 mm), and a Kodak Wratten 47B and 2A combination secondary filter were used. A circulating water bath to control the temperature at 38°, and a Sargent SR-G linear recorder was used for automatic readout.

Procedures

Assay of diamine oxidase. To 2.0 ml of tris buffer pH 9.5 were added 0.5 ml of cadaverine dihydrochloride (which gave a final concentration of 21.7 μg/ml), 0.1 ml of *p*-hydroxyphenylacetic acid (HPAA), and 0.1 ml of peroxidase. The fluorometer was set to zero. At zero time, a volume of diamine oxidase to be assayed was added, and the initial rate of reaction (ΔF/min) was recorded. From calibration plots of ΔF/min *vs.* diamine oxidase concentration, the amount of enzyme present was calculated.

Assay of monoamine oxidase. To 1.0 ml of tris buffer pH 8.8 were added 0.2 ml of benzylamine (which gave a final concentration of 100 μg/ml), 0.1 ml of HPAA, and 0.1 ml of peroxidase. The fluorometer was set to zero, and a volume of monoamine oxidase was added. The initial rate of production of fluorescence was measured, and the amount of monoamine oxidase was calculated from a calibration plot.

Determination of benzylamine, tyramine and furfurylamine. To 1.0 ml of tris buffer pH 8.80 were added a solution of the amine to be analyzed, 0.1 ml of HPAA and 0.1 ml of peroxidase. The fluorometer was set to zero. Then 0.5 ml of monoamine oxidase (9.90 units/ml) was added, and the initial rate of reaction was recorded as before.

Determination of cadaverine, histamine and putrescine. To 2.0 ml of tris buffer pH 9.5 were added a solution of the amine to be analyzed, 0.1 ml of HPAA, and 0.1 ml of peroxidase. The fluorometer was set to zero, 0.3 ml of diamine oxidase (70 units/ml) was added, and the initial rate was recorded.

TABLE I

ASSAY OF AMINES WITH DIAMINE OXIDASE

Cadaverine·2HCl (μg/ml)			*Histamine·2HCl (μg/ml)*			*Putrescine (μg/ml)*		
Added	*Found*[a]	*Relative error (%)*	*Added*	*Found*[a]	*Relative error (%)*	*Added*	*Found*[a]	*Relative error (%)*
0.289	0.286	−1.01	0.170	0.170	0.00	0.175	0.175	0.00
0.434	0.430	−0.92	0.342	0.340	−0.58	0.263	0.262	−0.38
0.720	0.750	+4.17	0.684	0.660	−3.51	0.350	0.345	−1.43
1.14	1.12	−1.75	0.855	0.860	+0.59	0.438	0.438	0.00
1.47	1.44	−2.08	1.03	1.00	−2.91	0.526	0.500	−4.94
Av. rel. error ±1.98			Av. rel. error ±1.52			Av. rel. error ±1.35		

[a] Represents 3 or more determinations with a relative standard deviation of ±2.0%.

TABLE II

ASSAY OF AMINES WITH MONOAMINE OXIDASE

Benzylamine (μg/ml)			*Tyramine·HCl (μg/ml)*			*Furfurylamine*		
Added	*Found*[a]	*Relative error (%)*	*Added*	*Found*[a]	*Relative error (%)*	*Added*	*Found*[a]	*Relative error (%)*
1.64	1.70	+3.66	3.33	3.50	+5.15	4.58	4.50	−1.75
2.46	2.41	−2.03	6.67	6.51	−2.40	5.50	5.10	−7.27
3.27	3.22	−1.53	10.0	10.5	+5.00	6.45	6.30	−2.33
4.91	4.80	−1.83	13.3	13.5	+1.50	7.33	7.70	+5.05
8.18	8.40	+2.69	16.7	16.0	−4.19	18.3	18.6	+1.64
16.4	16.4	+0.00	20.0	20.6	+3.00	27.5	26.3	−4.37
Av. rel. error ±1.95			Av. rel. error ±3.21			Av. rel. error ±3.74		

[a] Represents 3 or more determinations with a relative standard deviation of ±2.0%.

TABLE III

ASSAY OF MONOAMINE AND DIAMINE OXIDASE

Monoamine oxidase (units/ml)			*Diamine oxidase (units/ml)*		
Added	*Found*[a]	*Relative error (%)*	*Added*	*Found*[a]	*Relative error (%)*
0.330	0.310	−3.04			
0.670	0.650	−2.98	0.467	0.470	±0.64
1.00	1.00	0.00	0.700	0.660	−5.70
1.33	1.30	−2.26	0.935	0.940	+0.54
1.67	1.60	−4.19	1.16	1.14	−1.72
3.30	3.30	0.00	2.34	2.36	+0.85
6.70	6.70	0.00	4.67	4.60	−1.50
10.0	10.0	0.00			
Av. rel. error ±1.56			Av. rel. error ±1.83		

[a] Represents 3 or more determinations with a relative standard deviation of ±2%.

DISCUSSION AND RESULTS

General

By using nonlimiting amounts of peroxidase, *p*-hydroxyphenylacetic acid, and either monoamine oxidase or diamine oxidase, the initial rate of change of fluorescence (ΔF/min) was found to be directly proportional to the amine concentration.

The following amines could be determined with diamine oxidase by an initial rate method within 3–5 min (Table I): cadaverine (0.27–1.5 μg/ml), histamine (0.20–1.0 μg/ml) and putrescine (0.020–0.55 μg/ml).

With monoamine oxidase the following amines could be determined by an initial rate method within 3–5 min (Table II): benzylamine (1–16 μg/ml), tyramine HCl (2–25 μg/ml), and furfurylamine (4–30 μg/ml).

When nonlimiting amounts of *p*-hydroxyphenylacetic acid, peroxidase, and substrate were used, the enzyme could be determined. Monoamine oxidase (0.30–10.0 units/ml) could be determined with benzylamine, and diamine oxidase (0.30–5.0 units/ml) could be determined with cadaverine (Table III).

Specificity of enzymes

The specificity of monoamine oxidase has been summarized by BLASCHKO[18]. Primary and secondary amines are readily oxidized by amine oxidase, but the latter only if the substituent is a methyl group. Although the rate of oxidation of methylamino compounds is always high, the tertiary amines are always oxidized more slowly. In a homologous series $CH_3(CH_2)_nNH_2$, maximal rates are attained with amylamine and hexylamine. The most important naturally occurring substrates of amine oxidase carry cyclic substituents. They are benzylamine, tyramine, furfurylamine, and tryptamine. Tryptamine, although claimed to be a good substrate, failed to show any reaction with our monoamine oxidase preparation.

The specificity of diamine oxidase (DAO) has been summarized by ZELLER[19]. Alkylamines and their ω-hydroxy and bromo derivatives, benzylamine, tyramine, and mescaline are attacked by this enzyme. In general, high substrate concentrations and large quantities of the enzyme are required to demonstrate oxidative deamination of monoamines by DAO. Accordingly, the K_m values of diamines are about one-tenth those of the corresponding amines. Putrescine, cadaverine, 2-hydroxyputrescine, and 2-hydroxycadaverine are good substrates. The mono- and dimethyl derivatives of putrescine and cadaverine are highly useful substrates. Histamine is also a very good substrate.

Stability of enzymes

Peroxidase solutions containing 1 mg/ml are stable for over a year at 5°. Monoamine and diamine oxidase are not as stable, but if stored at $-5°$, the activity appears to be undiminished for a period of over 3 months.

Analysis of mixtures

Mixtures of amines can be analyzed, provided that one amine is a substrate for monoamine oxidase (benzylamine, tyramine or furfurylamine) and the other is a substrate for diamine oxidase (cadaverine, histamine or putrescine) and provided that

TABLE IV

EFFECT OF DIVERSE AMINES ON THE DETERMINATION OF AMINES

Concn. amine analyzed ($\mu g/ml$)	*Concn. diverse amine ($\mu g/ml$)*	*Rate ($\Delta F/min$)*
Cadaverine, 1.65	None	7.45
Cadaverine, 1.65	Benzylamine, 2.26	7.46
Cadaverine, 1.65	Benzylamine, 9.81	6.00
Cadaverine, 1.65	Benzylamine, 16.4	5.60
Cadaverine, 1.65	Benzylamine, 32.7	5.40
Cadaverine, 1.65	Tyramine, 1.42	7.45
Cadaverine, 1.65	Tyramine, 3.51	7.46
Cadaverine, 1.65	Tyramine, 17.6	6.90
Benzylamine, 13.0	None	1.30
Benzylamine, 13.0	Cadaverine, 16.6	0.40
Benzylamine, 13.0	Cadaverine, 33.1	0.35

the relative concentrations of the two amines are in the proper ratios. For example, a mixture of cadaverine and benzylamine can be analyzed if the concentration of the latter is less than 5 times that of cadaverine (Table IV). For cadaverine and tyramine this ratio can be as high as 1:10. Cadaverine will cause a great deal of inhibition in the benzylamine rate at equal concentrations of both amines, making the analysis of their mixtures impossible. However, when the cadaverine concentration is 1/3 lower than benzylamine, the analysis of the mixture is possible. Taking these limitations into account, it can be seen that mixtures can be done quite easily.

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SUMMARY

Fluorescence methods are described for the assay of the oxidative enzymes, monoamine and diamine oxidase. The method is based on the conversion of the non-fluorescent *p*-hydroxyphenylacetic acid to a highly fluorescent fluorophore by hydrogen peroxide and peroxidase. The initial rate of formation of this fluorescent compound is measured and related to the activity of the enzymes. The substrates of these enzyme systems—benzylamine, tyramine, furfurylamine, cadaverine, histamine, and putrescine—can be determined in microgram concentrations with a precision and accuracy of better than 3%. The reagent *p*-hydroxyphenylacetic acid is stable and can be used for several months.

RÉSUMÉ

On décrit des méthodes de fluorescence pour le contrôle d'enzymes, et d'oxydase monoamine et diamine. La méthode est basée sur la conversion de l'acide *p*-hydroxyphénylacétique, non-fluorescent, en un composé très fluorescent, par le peroxyde d'hydrogène et la peroxydase. La vitesse initiale de formation de ce composé fluorescent est mesurée et rapportée à l'activité des enzymes. Les substrats de ces systèmes d'enzyme—benzylamine, tyramine, furfurylamine, cadavérine, histamine et putrescine—peuvent être dosés en concentration de l'ordre du microgramme avec précision et exactitude (mieux que 3%). Le réactif, l'acide *p*-hydroxyphénylacétique, est stable et peut être conservé plusieurs mois.

ZUSAMMENFASSUNG

Es werden Fluorescenzmethoden zur Untersuchung der oxydativen Enzyme Monoamin- und Diaminoxydase beschrieben. Die Methode beruht auf der Umwandlung der nichtfluoreszierenden *p*-Hydroxyphenylessigsäure zu einem stark fluoreszierenden Fluorophor durch Wasserstoffperoxyd und Peroxydase. Die anfängliche Bildungsgeschwindigkeit dieser fluoreszierenden Verbindung wird gemessen und zur Aktivität des Enzyms in Bezug gesetzt. Die Substrate dieser Enzymsysteme, Benzylamin, Tyramin, Furfurylamin, Cadaverin, Histamin und Putrescin können in μg-Mengen mit einer Richtigkeit und Reproduzierbarkeit von besser als 3% bestimmt werden. Das Reagenz *p*-Hydroxyphenylessigsäure ist stabil und kann einige Monate lang benutzt werden.

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DOSAGE DU CUIVRE DANS LE SULFURE DE CADMIUM

F. CABANE-BROUTY
Laboratoire de Métallurgie, Faculté des Sciences, Centre de St. Jérôme, Marseille-13è (France)

(Reçu le 16 mai, 1969)

Les mesures physiques effectuées sur du sulfure de cadmium ont mis en évidence des variations de photoconduction, de photoluminescence liées à la présence de cuivre dans le matériau[1]. Toute étude systématique de ces phénomènes nécessite la détection et la mesure de la concentration en cuivre dans les produits utilisés. Le problème se pose alors sous deux aspects assez différents: d'une part détection et dosage éventuel du cuivre dans le sulfure de cadmium pulvérulent de haute pureté (99.999% nominale), d'autre part, mesure de la concentration réelle en cuivre des dépôts de sulfure de cadmium sur lesquelles seront faites des mesures électriques*.

Dans le premier cas, il s'agit de rechercher des traces de cuivre (le rapport pondéral Cu/CdS étant de l'ordre de 10^{-6} à 10^{-7}) dans des quantités assez importantes de produits (10 g); dans le second cas, les dépôts ont été généralement dopés avec du cuivre et contiennent théoriquement des concentrations en cuivre variables entre 10^{-4} et quelques 10^{-1}, le point délicat est alors que la quantité de matière disponible pour un dosage est très faible (4 à 40 mg).

Le problème ainsi posé, nous avons essayé de le résoudre à l'aide de deux techniques de spectrophotométrie: la colorimètrie et l'absorption atomique.

PARTIE EXPÉRIMENTALE

Etalons

Les deux méthodes envisagées nécessitent un étalonnage préalable pour déterminer ensuite la concentration d'un échantillon inconnu.

Les étalons ont été préparés à partir de sulfure de cadmium pulvérulent aussi pur que possible (99.999% avec concentration en cuivre de l'ordre de $0.1 \cdot 10^{-6}$) et de cuivre massif de pureté 99.999%. Les réactifs utilisés sont des produits Merck Suprapur. Le sulfure de cadmium est attaqué par l'acide chlorhydrique concentré et le cuivre par l'acide nitrique; le mélange en proportions convenables des solutions ainsi préparées conduit à une série d'étalons dont les caractéristiques sont réunies dans le Tableau I. Dans ce Tableau, les concentrations en cadmium et en cuivre des solutions obtenues, sont données en microgramme par millilitre.

Dosages par colorimètrie

Etalonnage. Dans le cas étudié, la grande quantité de cadmium susceptible d'être présent dans les solutions rend impossible l'utilisation des dosages colori-

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* Cette étude fait l'objet d'une convention passée entre le Centre National d'Etudes Spatiales et les Laboratoires de Métallurgie et de Photoélectricité de la Faculté des Sciences de Marseille.

TABLEAU I

SOLUTIONS ÉTALONS

I Solution de cadmium (μg Cd/ml)	$20\cdot10^4$	$4\cdot10^4$	$4\cdot10^3$	$4\cdot10^2$
II Solution de cuivre (μg Cu/ml)	0.5	1	5	10

III Solutions (cadmium + cuivre) préparées à partir de I et II (concentrations en μg/ml)

Cd	*Cu*	*Cd*	*Cu*	*Cd*	*Cu*	*Cd*	*Cu*	*Cd*	*Cu*
$3\cdot10^4$	0.04	$1.5\cdot10^4$	0.02	$0.8\cdot10^4$	0.03	$6\cdot10^3$	0.008	$3\cdot10^3$	0.04
	0.08		0.04				0.08		0.08
	0.2		0.1		0.2		0.4		0.2
	0.4		0.2		0.4				0.4
$1.5\cdot10^3$	0.01	$0.9\cdot10^3$	0.05	$3\cdot10^2$	0.04	40	0.05	0	0.1
	0.02		0.1		0.08		0.1		0.2
	0.08		0.25		0.2		0.25		0.5
	0.1		0.4		0.4		0.4		

métriques classiques du cuivre. De plus, ces dosages ne permettent pas d'atteindre la sensibilité recherchée.

Par contre, le dosage du cuivre par la biscyclohexanoneoxalyldihydrazone ou cuprizone[2-4], utilisée par d'autres chercheurs pour les milieux biologiques, les végétaux[5-7] et les métaux[8-11] a donné de meilleurs résultats. Le cuivre donne avec la cuprizone un composé bleu, stable en milieu basique (pH$\geqslant$8.5), fortement absorbant à la longueur d'onde de 600 nm. Un étalonnage fait avec des solutions contenant uniquement du cuivre montre que la loi de Lambert–Beer est vérifiée pour des concentrations variant de 0.05 à $2\cdot10^{-6}$ en poids (Fig. 1).

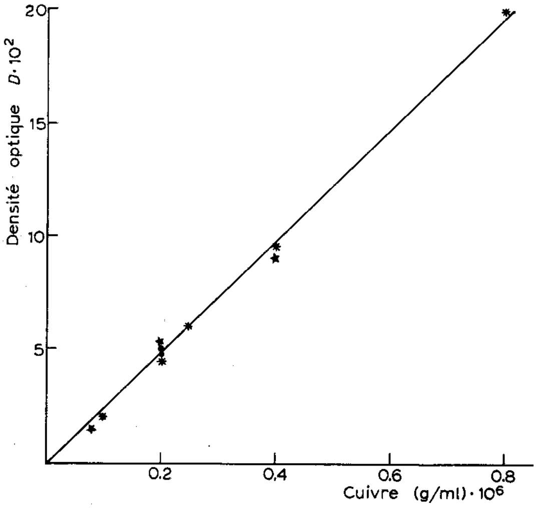

Fig. 1. Dosage du cuivre par colorimètrie. Etalonnage: D = f (concn. en cuivre) pour des solutions à teneurs variables en cadmium. (*) [Cd] = 0; (★) [Cd] = $3\cdot10^{-3}$ g/ml; (●) [Cd] = $3\cdot10^{-2}$ g/ml.

En milieu basique, on observe une précipitation du cadmium sous forme d'hydroxyde; pour éviter ce phénomène gênant, il suffit d'éliminer les ions Cd^{2+} en les complexant à l'aide de citrate d'ammonium. Dans ces conditions, les ions Cu^{2+} peuvent également être complexés; toutefois les mesures d'absorption faites sur des solutions de cuivre seul, en présence de citrate d'ammonium, sont identiques à celle de la courbe d'étalonnage (Fig. 1). On peut donc en conclure que si le complexe citrique du cuivre se forme au moment de l'addition de citrate, il est détruit pratiquement totalement en présence de cuprizone, le complexe cuivre–cuprizone étant vraisemblablement beaucoup plus stable. Des mesures ont été faites pour les solutions les plus concentrées en cadmium (Tableau I): elles donnent des valeurs identiques à celles de la courbe d'étalonnage de la Fig. 1. Il est donc possible d'effectuer des dosages du cuivre par la cuprizone en présence de grandes quantités de cadmium.

Dosages par absorption atomique

Des essais préliminaires nous ont montré que les meilleures conditions de dosage de très faibles quantités de cuivre étaient réunies lorsque la solution à doser avait un pH voisin de 7 et une quantité de sels dissous assez faible. Pour réaliser ces deux conditions, nous évaporons à sec les solutions obtenues après attaque acide; puis le résidu est repris par l'eau et la solution ajustée en fiole jaugée.

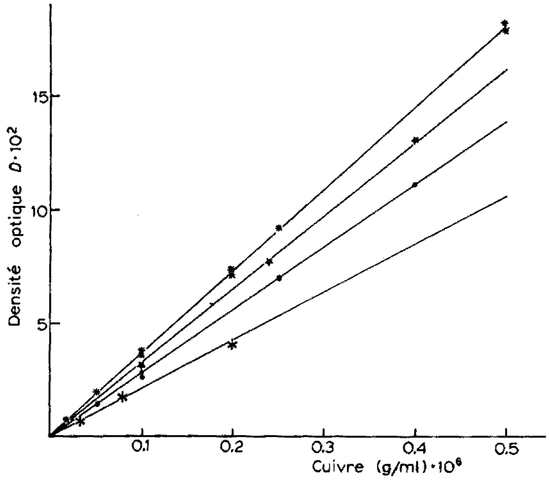

Fig. 2. Dosage du cuivre par absorption atomique. Etalonnage: D = f (concn. en cuivre) pour des solutions à teneurs variables en cadmium. (∗) [Cd] = 0; (★) [Cd] = $3\cdot10^{-4}$ g/ml; (●) [Cd] = 10^{-3} g/ml; (⋆) [Cd] = $3\cdot10^{-3}$ g/ml.

Les mesures sont faites directement sur les solutions ainsi obtenues. La lampe à cathode creuse de cuivre est alimentée avec un courant de 10 mA; la flamme est obtenue par un mélange air–acétylène, légèrement éclairant; les solutions atomisées sont préchauffées avant de passer dans la flamme. Le faisceau issu de la lampe traverse trois fois la flamme avant d'être reçu par le spectrophotomètre réglé sur la longueur d'onde 324.7 nm. La largeur spectrale de la fente utilisée est de 10 Å.

Des mesures faites sur plusieurs séries de solutions montrent (Fig. 2) que la loi de Beer–Lambert est vérifiée pour des concentrations de cuivre variant de 0.02 à

$2 \cdot 10^{-6}$, lorsque la concentration en cadmium est nulle ou lorsqu'elle est maintenue constante.

D'autre part on observe que la pente des droites d'étalonnage diminue avec l'augmentation de la concentration en cadmium. Lorsque la concentration en cadmium dépasse une certaine valeur ($5 \cdot 10^3$ p.p.m.) les mesures effectuées ne sont plus reproductibles. Par conséquent, à concentration constante en cuivre, l'absorption diminue quand la concentration en cadmium augmente. Ce phénomène ne peut être expliqué par des interférences entre le cuivre et le cadmium, bien qu'il existe pour ce dernier une raie à 325.02 nm très voisine de celle du cuivre.

En effet dans le cas d'interférence Cu–Cd, la loi de Beer–Lambert ne devrait pas être vérifiée dans des solutions où la concentration en cadmium est constante.
Une autre explication doit être donnée: la concentration croissante en cadmium provoque un refroidissement progressif de la flamme et par suite une diminution du rendement en atomes de cuivre absorbant. Ceci est en accord avec les résultats observés.

Il est donc possible de faire des dosages de cuivre en présence de cadmium par absorption atomique, à condition toutefois de faire un étalonnage avec des solutions de même teneur en cadmium.

RÉSULTATS ET CONCLUSIONS

Les principales caractéristiques des deux méthodes sont réunies dans le Tableau II.

TABLEAU II

CARACTÉRISTIQUES PRINCIPALES DES DEUX MÉTHODES

	Cuivre détectable (μg/ml)	*Cuivre mesurable à 5% (μg/ml)*	*Concn. Cd max. (μg/ml)*	*Cu/CdS détect. (g/g)*	*Cu/CdS mesurable à 5% près (g/g)*	*Prise d'essai minimum (g) (Cu/CdS = 10^{-5})*
Colorimètrie	0.04	0.1	$3 \cdot 10^4$	10^{-6}	$2.5 \cdot 10^{-6}$	0.4
Absorption atomique	0.004	0.04	$3 \cdot 10^3$	10^{-6}	10^{-5}	0.04

Sensibilité

Pour calculer la sensibilité de détection du cuivre dans le sulfure de cadmium, il faut tenir compte de deux facteurs, d'une part la sensibilité du dosage du cuivre dans la solution et d'autre part la teneur maximale en cadmium admissible dans la solution.

La spectrophotomètrie d'absorption atomique est environ 10 fois plus sensible que la colorimètrie compte-tenu des moyens dont nous disposons pour augmenter la sensibilité de l'appareillage: préchauffage de la solution, passages multiples du faisceau dans la flamme, dispositif d'expansion de l'échelle de mesure couplé à une constante de temps. Mais la concentration en cadmium admissible dans la solution étant nettement plus élevée lors des mesures colorimétriques, la sensibilité définie par le rapport massique Cu/CdS dans le solide est approximativement la même pour les deux méthodes envisagées, soit environ 10^{-6}.

Précision

La précision des mesures effectuées sur les solutions dépend d'un grand nombre de facteurs; en particulier, en absorption atomique, non seulement interviennent les bruits du système de détection et d'amplification du signal de mesure, mais également les différents réglages du dispositif de flamme. Toutefois en comparant les solutions inconnues à des solutions étalons de composition voisine, et en effectuant les mesures dans les mêmes conditions, on obtient facilement des résultats reproductibles avec une bonne précision. Dans le Tableau II, nous indiquons les concentrations mesurables avec une précision de l'ordre de 5% soit 0.04 μg/ml dans la solution et 10^{-5} g/g dans CdS; il s'agit ici, d'une précision obtenue après une ou deux mesures d'absorption effectuées lorsque l'appareillage a atteint son équilibre thermique; ceci présente un intérêt pratique puisque nous disposons souvent d'une faible quantité de solution (10 ml) et que nous envisageons la recherche de plusieurs éléments. Il est possible d'obtenir une meilleure précision en effectuant plusieurs passages de la solution dans la flamme et en encadrant chaque mesure inconnue par deux mesures connues; dans ces conditions la précision est de l'ordre de 2%.

En colorimètrie, une précision de 5% peut être obtenue pour une teneur minimale de 0.1 μg/ml dans la solution ce qui correspond à $2.5 \cdot 10^{-6}$ μg/ml de cuivre dans le sulfure de cadmium à la concentration maximale en cadmium.

Il apparaît donc que la colorimètrie donne de meilleurs résultats par suite des possibilités de travailler avec des solutions plus concentrées en cadmium.

Choix d'une méthode

En dehors des critères précédents qui sont favorables au dosage du cuivre dans le sulfure de cadmium par colorimètrie, nous devons envisager plusieurs autres facteurs avant de choisir le dosage le mieux adapté aux circonstances. Tout d'abord, nous avons indiqué dans le Tableau II, la quantité minimale de substance nécessaire pour effectuer à l'aide des deux méthodes un dosage dans des conditions voisines; nous constatons qu'il faut beaucoup moins de matière pour l'absorption atomique que pour la colorimètrie.

De plus la préparation de la solution en vue du passage dans la flamme est très simple, ce qui diminue les risques de contamination, non négligeables quand on veut doser des traces. Enfin la solution ainsi préparée pour le dosage du cuivre peut être utilisée directement pour la recherche et le dosage d'autres éléments par absorption atomique, problème beaucoup plus délicat dans le cas de la formation du complexe cuivre–cuprizone.

Conclusion

Les deux méthodes spectrophotomètriques étudiées permettent de rechercher et de doser de faibles quantités de cuivre présent comme impureté ou élément dopant dans du sulfure de cadmium solide. Etant données la simplicité et la rapidité des dosages par absorption atomique, cette méthode est préférable malgré un étalonnage un peu délicat. Son utilisation est impérative lorsqu'on dispose de très faibles quantités de substances et si l'on envisage la recherche de plusieurs éléments à partir du même échantillon. Par contre la colorimètrie est mieux adaptée à la recherche et à la mesure de très faibles quantités de cuivre dans le sulfure de cadmium lorsqu'on dispose de quantités suffisantes de substance.

RÉSUMÉ

Le dosage du cuivre dans le sulfure de cadmium a été envisagé par deux méthodes: colorimètrie du complexe cuivre–cuprizone et absorption atomique. Des concentrations en cuivre de l'ordre de 10^{-6} g par g de sulfure de cadmium pour la colorimètrie et de 10^{-5} g pour l'absorption atomique sont mesurables sans difficultés avec une précision de 5%. Dans le cas des plus faibles concentrations et lorsqu'on dispose de quantités de produit peu importantes (inférieures à 40 mg), seule l'absorption atomique est utilisable.

SUMMARY

Two methods are described for the determination of copper in cadmium sulphide. Copper concentrations of the order of 10^{-6} g per g of cadmium sulphide can be determined spectrophotometrically by means of the cuprizone complex, whereas 10^{-5} g/g can be determined by atomic absorption spectrophotometry, with a precision of about 5%. For smaller amounts, or when the sample size is limited (<40 mg), atomic absorption spectrophotometry must be used.

ZUSAMMENFASSUNG

Es werden zwei Methoden zur Bestimmung von Kupfer in Cadmiumsulfid beschrieben. Kupferkonzentrationen von 10^{-6} g/g CdS können spektralphotometrisch mit dem Cuprizon-Komplex bestimmt werden, während 10^{-5} g/g mit der Atomabsorptionsspektroskopie mit einer Genauigkeit von etwa 5% ermittelt werden kann. Bei kleineren Mengen, oder wenn die Probengrösse begrenzt ist (<40 mg), muss die Atomabsorption verwendet werden.

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DECOMPOSITION BY PRESSURE IN INORGANIC ANALYSIS

J. DOLEŽAL, J. LENZ AND Z. ŠULCEK
Department of Analytical Chemistry, Charles University, Prague, and Research Institute of Electrotechnical Ceramics, Hradec Králové, and Central Geological Institute, Prague (Czechoslovakia)

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In some industries, for example the atomic and electronic industries (manufacture of semiconductors, piezoceramics, single crystals, etc.) very severe demands are made on analytical laboratories, not only with respect to the precision and accuracy of the methods used but also their sensitivity and selectivity. Classical analytical methods have been largely replaced by highly sensitive physico-chemical methods, most of which necessitate complete dissolution of samples. It is this basic operation—conversion of the original sample to a solution—which is a major source of errors and difficulties. Accordingly, numerous authors have sought alternative means of decomposition, and increasing attention has been paid to decomposition procedures at elevated pressures; such methods have been known for a long time, but have only recently received much notice.

Decomposition methods at elevated pressures may be classified in two groups:

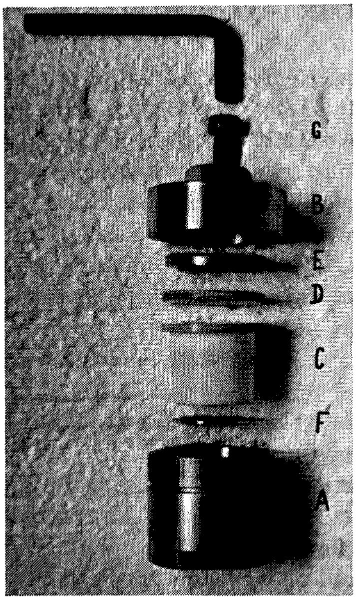
1. decomposition in sealed ampoules of special glass,
2. decomposition in an autoclave, lined with platinum or polytetrafluoroethylene (PTFE, Teflon). The advantage of the first technique is the simplicity of the equipment, but it does not permit the determination of alkalis, silicon and other elements contained in glass. Moreover, hydrofluoric and phosphoric acids, as well as concentrated alkali hydroxide solutions, cannot be employed. These decomposition methods have been studied by WICHERS *et al.*[1,2] and by NOVÁK[3].

In the present work, the autoclave type of decomposition was examined. The first tests involved the techniques described by ITO[4] and other authors[5–10], who decomposed mineral materials by a stationary process, *i.e.* without agitating the reaction mixture. Under these conditions, decomposition proved to be lengthy and the reaction rate decreased owing to the formation of reaction products on the sample surface. Moreover, some types of autoclave[4,5] were found unsuitable for routine use.

The purpose of the present work was mainly to design a new pressure apparatus, in which the decomposition process could be speeded by continuous agitation under defined temperature conditions, and to verify the efficiency of decomposition of highly resistant substances.

CONSTRUCTION OF APPARATUS

The apparatus developed is shown in Figs. 1 and 2. The autoclave consists of a steel mantle (A), sealing lid (B), PTFE crucible (C) with lid (D), sealing inlay (E) and an elastic steel inlay (F) which presses upward. The seal consists of a thrice-interrupted thread and imbus-type bolt (G) which seals the crucible space hermetically by pressing onto the elastic inlay. The mantle bottom is fitted with a threaded hole serving to screw the autoclave onto the bolt (I) of the manipulation plate (J): this facilitates the removal of the PTFE crucible from the autoclave after the decomposition process is complete, the elastic inlay protecting the bottom of the PTFE crucible from damage. A PTFE foil about 0.1 mm thick is placed between the crucible and the inlay to decrease the danger of contamination of the crucible lid and bottom surfaces by oxidation products of the steel of the two inlays. The autoclave is taken out of the heating box, which is described later, by means of tongs (K). For opening and clos-



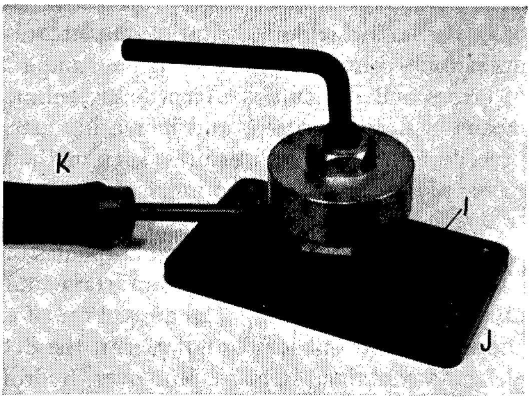


Fig. 1. Autoclave with teflon crucible for pressure decomposition.

Fig. 2. Handling plate for removal of crucibles from autoclaves.

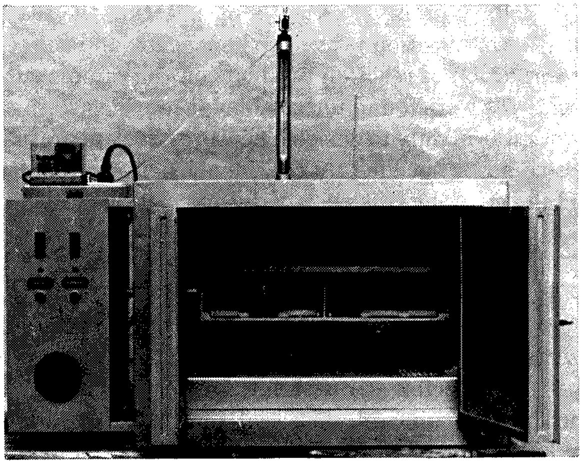


Fig. 3. Oven for pressure decomposition for routine analysis.

ing, the autoclave is fitted to the respective slot of the manipulating plate which can be screwed to the laboratory bench.

The PTFE crucible has a capacity of 25–30 ml; the internal diameter is 30 mm, the height is 40 mm and the wall thickness 8 mm. When PTFE crucibles and cylinders are made, it is best first to machine them roughly to size, and then to heat them to 245° for about 12 h, before the final machining to the exact dimensions after cooling. In this way, shrinking of the finished crucibles is avoided when they are first used.

Spraying the inner surface of the autoclave with a PTFE suspension (Teflon-Sprüh) was also found useful. The thin PTFE layer completely eliminates the danger of contamination of the crucibles with oxidation products of the autoclave steel. For routine work a special oven (Fig. 3) was designed; this allows handling of six autoclaves at a time and ensures sufficient agitation of the reaction mixture. An electric motor rotates a robust frame to which the autoclaves with the samples are fixed simply by means of wing screws. The frame rotates at about 60 rev/min. The frame is fitted in PTFE bearings which eliminate the need of lubrication. The box is heated by three resistance heaters (500 W each); the optimum temperature of 240° is maintained by means of a relay system after setting to ± 2° on a contact thermometer.

RESULTS

Pressure decomposition of corundum

High-purity corundum is a basic raw material for making corundum ceramics. The material must be analysed for impurities, mainly SiO_2, Fe_2O_3, TiO_2, CaO, MgO, Na_2O and K_2O. Corundum has generally been decomposed by fusion with potassium pyrosulphate, dissolution in a mixture of hydrofluoric and sulphuric acids and fusion of the residue with a sodium carbonate–borax mixture[11]. The analyses are rather laborious and the results are subject to a large degree of deviation because of the small amounts of admixtures determined. This applies especially to alkalis, the decomposition of which is not quantitative especially with corundum which has been calcined at high temperatures. Accordingly, WICHERS *et al.*[12] recommended a high-pressure decomposition of sintered corundum with concentrated hydrochloric acid in a sealed ampoule at 260°, the decomposition taking 15 h; in another case, these authors found a decomposition temperature of 300° for a period of 25 to be necessary. A comparable decomposition carried out at atmospheric pressure in an open vessel was very inefficient, and this was also true for decomposition with nitric acid. NOVÁK[3] mentions a successful pressure decomposition of corundum single crystals in 5–7 *N* hydrochloric acid at 230° for 24 h. ITO[4] decomposed corundum with a mixture of sulphuric and hydrofluoric acids (1 + 1) for 4 h at 240°. WAHLER[6] mentions the difficulty of similar decompositions, in which mixtures of hydrofluoric and perchloric acid were used at 200°. This temperature does not suffice for complete decomposition, as will be shown later. WEIBEL[13] recommends hydrofluoric acid alone, while other authors[14] suggest a mixture of sulphuric and phosphoric acids.

Various pressure decompositions were carried out on the basis of these data, as summarised in Table I. The survey shows that hydrochloric acid, which some authors recommend[2,3], is less efficient than dilute sulphuric acid. Likewise, perchloric acid is not suitable for decomposition. For complete and rapid decomposition of corundum with hydrofluoric acid at elevated pressure, the mixture must be agitated continu-

TABLE I

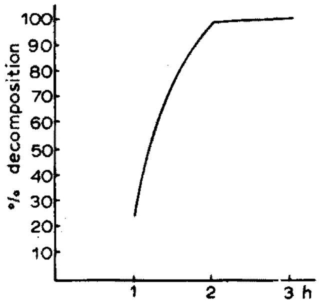
PRESSURE DECOMPOSITION OF α-Al_2O_3 WITH THE USE OF DIFFERENT AGENTS AT 240°

Decomposition agent[a] *(ml)*	*Time of decomposition(h)*	*Percentage decomposition*[b]	*Note*
15 HF	4	$<$30–50	Stationary decomposition
8 HF; 8 H_2SO_4(1 + 1)	4	$<$30–50	Stationary decomposition
8 HF; 8 H_2SO_4(1 + 1)	5	$<$30–50	Stationary decomposition
8 HF; 8 HCl(1 + 1)	5	$<$30–50	Stationary decomposition
15 HCl conc.	3.5	96.9	With agitation
15 HCl(2 + 1)	3	95.7	With agitation
15 HCl(1 + 1)	4	96.5	With agitation
15 $HClO_4$(1 + 1)	3.5	88.4	With agitation
15 HF	3.5	100.0	With agitation
15 HF; 3 $HClO_4$	3.5	100.0	With agitation
5 H_2SO_4(1 + 1); 5 H_3PO_4	4.5	100.0	With agitation
15 H_2SO_4(2 + 1)	3	100.0	With agitation

[a] Amounts stated apply to 0.50 g Al_2O_3; sample ground to below 0.063 mm.

[b] The degree of decomposition was determined gravimetrically by weighing the undecomposed portion of the sample or after volatilising silica with hydrofluoric and sulphuric acid.

ously. Sulphuric acid, however, is more advantageous from the analytical point of view. Mixtures of sulphuric and phosphoric acids can be used in those exceptional cases where sulphuric acid alone is not completely effective, as in the case of special corundum ceramics. In the case of sulphuric acid, the dependence of the degree of decomposition on the duration of the process was studied. The results are shown in Fig. 4, which shows that corundum is quantitatively decomposed within 3 h. For routine analyses this time was prolonged by another 30–60 min.



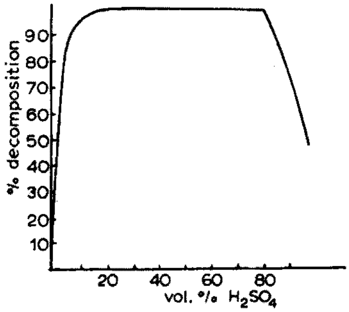


Fig. 4. Degree of decomposition of corundum related to the time needed (0.5 g of corundum and 17 ml of 2 + 1 sulphuric acid).

Fig. 5. Influence of sulphuric acid concentration on the completeness of decomposition of corundum (0.5 g of corundum and 15 ml of sulphuric acid; decomposition time 3.5 h).

The dependence of the extent of decomposition on the sulphuric acid concentration was also investigated (Fig. 5). It was found that 30–70% sulphuric acid may be used with the same result. In practical cases sulphuric acid diluted 1+1 with water is most convenient.

Since the decomposition temperature employed (240°) is practically at the limit of usability of PTFE crucibles, it was essential to find out whether corundum could be decomposed at a lower temperature. The results of the experiments (Fig. 6) indicate that a temperature decrease is accompanied by a lower degree of decomposition of the sample (*ca.* 1% for each 10°). These results agree with other experience on incomplete decomposition of materials at lower temperatures.

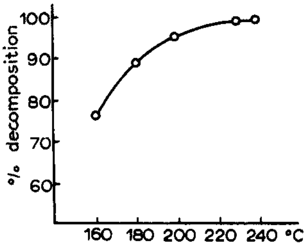


Fig. 6. Effect of temperature on decomposition of corundum (0.5 g of corundum and 15 ml of 1 + 1 sulphuric acid; decomposition time 3 h).

The preceding thermal processing of corundum substantially influences the efficiency of pressure decompositions. Accordingly, samples calcined at temperatures of 1400–1700° were decomposed and their specific surface area was measured by means of the Nelsen–Eggerts nitrogen adsorption method[15]. Samples (1 g) were pressure-decomposed with 15 ml of 1+1 sulphuric acid, with the results shown in Table II. These results show that the specific surface area of the samples decreases with rising calcination temperature, which also influences the degree of decomposition. A substantial decrease in the degree of decomposition of corundum is shown only in the case of a sample calcined at 1700° (by about 26%). According to previous results[9] recrystallisation takes place at this temperature, connected with crystal growth. It was proved by additional experiments that this type of corundum may also be decomposed with success by prolonging the decomposition time by some 30%. For this reason, the thermal history of the material should be known for practical analyses.

TABLE II

INFLUENCE OF THE THERMAL HISTORY OF α-Al_2O_3 ON COMPLETENESS OF PRESSURE DECOMPOSITION AT 240°

Calcination temperature (°)	*Specific surface (m^2/g)*	*Decomposition time (h)*	*Percentage decomposition*
1400	2.76	3	99.3
1500	1.47	3	98.8
1600	0.78	3	98.6
1700	0.50	3	73.1
1700	0.50	4	99.5

The influence of particle size on the degree of decomposition was also investigated, the other conditions being kept constant. It was found that excessively finely ground corundum (passing a sieve of 16,000 mesh/cm²) is more difficult to decompose than the same material ground to the conventional particle size (*ca.* 9600 mesh/cm^2); in this case, the reaction time was 30% longer.

The pressure decomposition of corundum with 30% sodium and potassium hydroxide solution was also tested: a 1-g sample was completely decomposed by 15 ml of 30% (w/v) potassium hydroxide solution after 4 h. Alcoholic hydroxide solutions may also be used. Alkaline decomposition was applied to the determination of silicon dioxide by the molybdenum blue method[9,10]. The pressure decomposition technique is especially suitable for this case, as the silicon dioxide obtained is essentially in the monomeric state, which is essential for the success of the method mentioned. A similar decomposition was examined for the preparation of a standard silicon dioxide solution, the starting material being very pure natural Brazilian silica. A 5-h period sufficed for complete dissolution of 1 g of silicon dioxide in 15 ml of 30% potassium hydroxide.

The above-mentioned procedure for the decomposition of corundum by means of sulphuric acid may be utilised in the flame-photometric determination of alkali metals, the spectrophotometric determination of iron and titanium, and the emission spectrographic determination of calcium and magnesium in solution. For the determination of silicic acid, alkaline decomposition of corundum with potassium hydroxide is better[10].

The decomposition of some electroceramic materials based on corundum of the spinel type ($MgO \cdot Al_2O_3$) and porcelain with a high corundum content was also investigated. Samples (0.3 g) of the corundum material were completely decomposed with 15 ml of a 12+1 mixture of sulphuric and perchloric acids within 10 h; mullite (0.4 g) was decomposed with 15 ml of a 2+1 mixture of phosphoric and hydrofluoric acids after 6 h, whereas the porcelain material with a high corundum content (0.5 g) was completely decomposed with 15 ml of a 2+1 mixture of phosphoric and hydrofluoric acids within 3 h.

Silicon dioxide

The decomposition of pure silica was mentioned above. Another important industrial material is sand for glass-making (silica with a low content of colouring oxides). The relatively high scatter of analytical results, especially in the case of iron, is usually ascribed to incomplete decomposition and to impurities introduced while grinding the sample or dissolving it. These difficulties may be eliminated by using pressure decomposition. A 4+1 mixture of hydrofluoric and perchloric acids was found to decompose glass-making sand completely within 10 h, 15 ml of the acid mixture being used per 1 g of the sample. A 13+2 mixture of hydrofluoric and sulphuric acids was found equally suitable. The main advantage of these pressure decompositions lies in the fact that the sample need not be ground before the decomposition operation (the sand analysed had a particle size of about 1 mm).

Tin dioxide

Synthetic tin dioxide with a cassiterite structure is an important raw material in the field of special electroceramics, the physical properties of the material being influenced mainly by the presence of Pb, Bi, Sb, Cu, Fe, SiO_2 and a number of other impurities. Among the decompositions described for natural tin dioxide, reducing fusion with sodium carbonate and cyanide, sulpho-alkaline decomposition, and fusion with sodium carbonate mixed with borax or sodium peroxide[11] should be mentioned.

The decomposition by mineral acids is not usually very efficient. WICHERS *et al.*[12] and NOVÁK[3] have described pressure decompositions with hydrochloric acid in glass ampoules, but even this method is unsatisfactory.

None of the above decomposition procedures is suitable for the purpose under discussion, since the corrosion products of the vessels employed make it impossible to determine the impurities mentioned. The problem can be solved completely by pressure decomposition in a teflon vessel, with dilute mineral acids. At elevated pressure and temperature (240°) , tin dioxide easily dissolves in hydrochloric or hydrobromic acid. Complete decomposition of 2 g of tin dioxide is achieved within 6 h with 15 ml of 38% hydrochloric acid or 48% hydrobromic acid. After volatilisation of tin(IV) bromide, all the trace components mentioned can be determined with a high precision.

Natural tin dioxide, cassiterite, behaves similarly to the synthetic material. Cassiterite (0.5 g) can be dissolved at elevated pressure in 15 ml of concentrated hydrochloric acid during 7 h. The dissolution of cassiterite will be discussed in a separate study: it is probable that the reducing effect of hydrochloric acid plays an important role in the decomposition process.

Another part of the study was devoted to investigating the pressure decomposition of some inorganic substances which are difficult to decompose, as well as of some resistant minerals and rocks. The results are summarised in Table III. The extent of decomposition is stated as percentage by weight of the material analysed. In cases where the undecomposed portion contained precipitated silica, the residue was volatilised with hydrofluoric and sulphuric acid and weighed again after ignition.

DISCUSSION

The pressure decomposition of inorganic substances carried out in the apparatus suggested by different authors[1–8] is done under stationary conditions, *i.e.* without the possibility of agitating the reaction mixture during the decomposition process. Under these conditions, the reaction products formed accumulate on the phase boundary in the decomposition of some substances (*e.g.* corundum), diffusion processes are slowed down, and insoluble films are formed which envelop the undecomposed material; all these processes cause incomplete decomposition. These various possible sources of error may explain some contradictory data on the decomposition of a number of inorganic compounds; sometimes, however, different reactivities of the same substance may be caused by differences of isomorphic admixtures or the preceding heat treatment of the sample.

The oven with automatic temperature control (usually 240°) and the device which causes continuous agitation of the reaction mixture in the autoclave during the decomposition process, as suggested in the present study, make it possible to improve the efficiency of decomposition with acids and also allow the reaction time needed for complete dissolution of the material to be decreased. With inorganic substances which have been ignited to high temperatures, the suggested procedure is practically the only possibility of completely dissolving these resistant compounds in mineral acid solutions.

The design of the autoclave is based on the concepts of several authors[4–7]; the main purpose was to achieve an apparatus which should be simple to operate, and

TABLE III

DECOMPOSITION OF SOME MINERALS, ORES, ROCKS AND OTHER RESISTANT SUBSTANCES[a]

Sample	*Weight (g)*	*Decomposition agent*[b] *(ml)*	*Decomposition time (h)*	*Percentage decomposition*	*Note*
Andalusite	0.5–0.8	16 H_3PO_4; 7 HF	6	100	Decomposition with H_2SO_4 or mixtures with HF is incomplete (< 30 %)
	0.8	10 $HClO_4$; 10 HF	5	46.5	
Beryl	0.3	20 HF	10	100	
	0.3	10 HF; 10 H_3PO_4	4	100	
Chromite	0.8	12.5 H_2SO_4(2 + 1) 12.5 HF	5	99.2	
Cr-ore	0.5–1	12 H_2SO_4(2 + 1); 12 HF	5	100	Oxidation $Cr^{III} \rightarrow Cr^{VI}$
	0.5	2.5 $HClO_4$; 8.5 HF	3.5	91.3	
CeO_2	1	25 HNO_3	3	100	
	1–5	25 HCl	3	100	
	1	25 $HClO_4$(60 %) + 0.1 HNO_3	3	100	
TiO_2 synth. anatase	0.5–1	25 H_2SO_4	13	100	After completion of pressure decomposition, dilute with exactly 15 ml H_2O, add 1–5 ml H_2O_2 and heat on water bath until complete dissolution
Rutile, synth.	1.2	22 H_2SO_4	5	99.6	
	0.5	22 H_2SO_4	16	100	
Magnetite	0.5	20 HBr	10	>99.5	SiO_2 found in the residue not volatilised with HF
	0.7	14 HBr; 1 HF	10	100	
	0.6	20 H_2SO_4(70 %)	6.5	100	
Pyrite	0.5	25 H_2SO_4	3	99	Residue contained SiO_2 and elementary sulphur; SO_2 was liberated from the reaction mixture
	0.6	20 H_2SO_4 + 1 ml Br_2	6.5	99.8	
Spinel, synth.	0.3	12 H_2SO_4(2 + 1);1 $HClO_4$	10	99.6	
	0.3	15 H_2SO_4	3	51.5	
Staurolite	0.6	14 H_3PO_4; 7 HF	4.5	100	
	0.5	16 HF; 4 $HClO_4$	3	46	
$SrTiO_3$, synth.	0.3	25 HCl	2	100	
$BaTiO_3$	0.3–0.5	25 HCl	4	100	
Tourmaline	0.5	12.5 H_2SO_4(1 + 1) 12.5 HF	3.5	100	
Zircon	0.5	25 HF	5	< 50	Incomplete decomposition even with HF mixed with H_3PO_4 or H_2SO_4 or $HClO_4$

TABLE III (*Continued*)

Sample	*Weight (g)*	*Decomposition agent*[b] *(ml)*	*Decomposition time (h)*	*Percentage decomposition*	*Note*
ZrO_2, synth.	0.6	12.5 H_2SO_4; 12.5 HF	4	100	
Augite		15 HF	13	100	
Nickel ferrite	0.2	15 HCl	6	100	
Ilmenite	1	15 H_2SO_4(65 %)	3	100	
Microcline	0.5	15 HF	13	99	
Rh powder metal	1	10 HCl; 1 $HClO_4$	10	100	
Titanite	0.5	7.5 HF; 5 H_2SO_4(1 + 1)	5.5	92	
Boron nitride	0.03	4 H_2SO_4 5 *M*	6	Full	For N_2 determination
Algonkian slate	0.2	10 H_3PO_4; 1 HF	8	100	
Lepidolite	0.5	20 H_2SO_4(1 + 1)	8	99	Ca found in the residue by means of spectral analysis

[a] Particle size of all materials below 200 mesh.
[b] Concentration of acids used: HF 38%, H_3PO_4 85%, $HClO_4$ 70%, HCl 37%, HNO_3 65 %.

suitable for routine work with the minimum danger of introducing impurities into the samples during the necessary operations. These conditions are satisfied by the apparatus suggested, which allows simultaneous decomposition of at least six samples, without supervision.

The pressure decomposition of corundum was most suitably carried out with 30–70% sulphuric acid; the dependence of the percentage decomposition on temperature explains the unsuccessful work of some authors carried out at lower temperatures. Any thermal pretreatment of the corundum sample slows down the decomposition process so that the reaction time must be prolonged by about 30%. The decomposition of corundum with dilute sulphuric acid as described was used for the determination of alkali metals (Table IV), iron, titanium, calcium, magnesium, etc. The results mentioned indicate that alkali values obtained by the pressure decomposition technique are higher than similar values obtained after conventional decomposition procedures. This difference is a systematic one and cannot be ascribed to random errors. Higher values indicate complete decomposition of the corundum sample at elevated pressures

TABLE IV

DETERMINATION OF SODIUM AND POTASSIUM IN CORUNDUM

Sample no.	*Na_2O(%)*		*K_2O(%)*	
	A[a]	*B*[b]	*A*[a]	*B*[b]
1	0.08	0.10	0.008	0.01
2	0.22	0.30	0.09	0.01
	0.20	0.33	0.008	0.01
	0.23	0.34	0.01	0.02
3	0.06	0.08	0.017	0.025
	0.06	0.08	0.018	0.020
	0.04	0.08	0.015	0.025
4	0.12	0.16	0.008	0.01
	0.10	0.16	0.006	0.011

[a] Usual sample decomposition with acids.
[b] Pressure decomposition.

and temperatures compared to incomplete conventional decomposition with mineral acids. Pressure decomposition with 30% potassium hydroxide solution was applied to the determination of small amounts of silicic acid. This technique leads to optimum conditions for the spectrophotometric determination of silicon by the molybdenum blue method since monomeric silicic acid is formed. A similar procedure may be used to decompose pure natural silica, and to prepare standard silicate solution with a decreased risk of contamination from grinding equipment, because particle size can be *ca.* 1 mm.

In the proposed method, the degree of contamination of the sample during its dissolution can be kept to a minimum, because larger particle sizes can be handled and there is no exchange of elements between sample and container, such as occurs in fusion procedures. These features can be of particular importance in the assessment of sands for glass-making; accompanying tourmaline, chromite, etc. are completely decomposed under the described conditions. The fact that "blank" determinations are minimal leads to greater precision of measurement, especially in the determinations of Fe, Al, Ti, Mg, Ca, Na, K, etc.

SUMMARY

A suitable apparatus for pressure decomposition of refractory inorganic materials with acids is described. The materials are heated under pressure in a steel autoclave lined with a PTFE crucible in a thermostatted oven fitted so that the autoclaves can be rotated. The decomposition process is hastened not only by pressure but also by continuous agitation. The decomposition of corundum was studied in detail. The proposed decomposition method was successfully applied to the analysis of titanium and tin dioxides, ferrites, boron nitride and several resistant rocks and minerals. Different acid mixtures are recommended for different materials; a pure silicon dioxide solution was easily prepared by pressure dissolution with potassium hydroxide. The methods are very suitable for routine use.

RÉSUMÉ

On décrit un appareil pour la décomposition sous pression de substances minérales réfractaires. Le processus de décomposition est activé non seulement par pression, mais également par agitation continue. On examine en détail la décomposition du corindon. Cette méthode a été appliquée avec succès à l'analyse des dioxydes de titane et d'étain, des ferrites, du nitrure de bore et plusieurs autres minerais. Différents mélanges d'acides sont recommandés suivant les produits: on peut obtenir facilement une dissolution de dioxyde de silicium pur par traitement à l'hydroxyde de potassium sous pression. Ces méthodes conviennent très bien aux travaux de routine.

ZUSAMMENFASSUNG

Es wird eine geeignete Apparatur für die Zersetzung schwer löslicher anorganischer Stoffe mit Säuren unter Druck beschrieben. Die Materialien werden unter Druck in einem Stahlautoklaven, der in Rotation versetzt werden kann, erhitzt. Die

Zersetzung von Korund wurde näher untersucht. Die vorgeschlagene Methode konnte erfolgreich für die Analyse von Titan- und Zinndioxid, Ferriten, Bornitrid und einiger widerstandsfähiger Steine und Mineralien angewandt werden. Unterschiedliche Säuremischungen eignen sich für verschiedene Materialien. Siliciumdioxid konnte leicht durch Behandeln mit Kaliumhydroxid unter Druck gelöst werden. Die Methode eignet sich für Routineuntersuchungen.

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CHEMICAL IMPRECISION IN THE SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH DITHIO-OXAMIDE

PETER JAMES LINGANE
Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455 (U.S.A.)

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With the exception of fluorimetric and radiochemical methods, analytical schemes for ruthenium usually must begin with its separation. Fortunately, ruthenium can be separated from nearly all other elements as the volatile tetroxide. The determination of the ruthenium content of the receiving solution is usually done spectrophotometrically using one of a variety of color-forming reagents. When high accuracy is required, the ruthenium may be isolated from the receiving solution by precipitation with thionalide or as the hydrous oxide. Since neither of the precipitates is a suitable weighing form for ruthenium, they are weighed as the metal after reduction in a stream of hydrogen at 600–700°[1].

Because few younger chemists have had significant experience with ignitions in hydrogen, it seemed desirable to investigate the possibility of achieving an equal precision with existing spectrophotometric methods by making the measurements differentially[2–12]. Dithio-oxamide (rubeanic acid) was selected as the color-forming reagent. As will be seen, this proved to be a poor choice.

Since the accuracy of a differential spectrophotometric method is no better than that of the standard (reference) solution, a convenient and accurate method for the preparation of such a solution is a prime consideration. A few ruthenium salts have been prepared in reasonable purity, notably K_2RuCl_5OH[13], and while these are sometimes used for the preparation of standards, it is the usual practice to analyze these salts before their use. Ruthenium tetroxide can and has been used as a primary standard for the preparation of solutions of ruthenium[14] but the ease with which it is reduced can make the preparation of ampules of ruthenium tetroxide a frustrating experience.

This study demonstrates the feasibility of preparing standard solutions of ruthenium by dissolving weighed portions of the pure metal powder in alkaline sodium hypochlorite[15]. The principal advantage to the dissolution of ruthenium in hypochlorite rather than in an alkaline peroxide flux (ruthenium is not attacked by strong acids or by *aqua regia*) is the fact that the solution remains sufficiently translucent that any metal remaining undissolved is clearly visible; the fused melt is opaque.

EXPERIMENTAL

Chemicals

Ruthenium metal powder (Johnson, Matthey, and Co., Ltd., c/o Matthey

Bishop Co., Malvern, Pa) contained 13 p.p.m. of spectroscopically determined impurities.

Standard solutions of ruthenium. These were prepared by dissolving accurately weighed 50-mg or 100-mg portions of this powder in sodium hypochlorite. The sodium hypochlorite solution was prepared by saturating a solution of chilled 1 *M* sodium hydroxide with chlorine; the solution was then swept with argon to remove most of the excess chlorine and the pH was adjusted with solid sodium hydroxide to about 10.5. 50 mg of ruthenium powder dissolve overnight in 100 ml of a solution prepared in this fashion.

After dissolution, the ruthenium solution was chilled and a chilled solution containing 50 ml of concentrated hydrochloric acid and 20 ml of 30% hydrogen peroxide was added; the addition was done cautiously as there was considerable gas evolution. The visible spectrum of these solutions indicated that the ruthenium was reduced principally to the +4 dimer. The solution was warmed to destroy the peroxide, then boiled gently to reduce the volume and also to remove some of the hydrochloric acid. The ruthenium concentration was approximately 2 m*M* after dilution to volume.

These conditions for the dissolution of ruthenium represent a balance of several factors. Apparently, hypochlorite reacts with ruthenium powder to produce ruthenium tetroxide which subsequently decomposes first to perruthenate (RuO_4^-) and, in alkaline solution, to ruthenate (RuO_4^{2-}) with the production of oxygen. Ruthenium tetroxide has a high vapor pressure over hypochlorite solutions unless they are strongly alkaline[15] and consequently the system must be equipped with a scrubbing system if ruthenium is not to be lost. A 250-ml iodine flask serves well for the reaction vessel and a satisfactory washing tower may be constructed from a standard tapered joint and a 20-mm coarse frit; 10 ml of 1 *M* sodium hydroxide placed in this washing tower effectively scrub the evolved gases. Ruthenium tetroxide has an odor much like that of ozone so that the efficiency of the scrubber is easily monitored. (Caution: The physiological effects of ruthenium tetroxide are not well documented but it is generally considered a hazardous substance.)

The dissolution cannot be carried out in a strongly alkaline solution because the rate of the oxidation of ruthenium metal is very slow. Neutral solutions are also unsatisfactory because the rate of the reaction is nearly explosive and because the product of the reaction is sodium perruthenate; it, unlike sodium ruthenate, is only slightly soluble.

Dithio-oxamide. The reagent (Aldrich Chemical Co., Milwaukee, Wisconsin) was recrystallized from ethanol before use.

The water was obtained by distillation of deionized water. Other chemicals were of reagent quality and were not further purified.

Apparatus

Since the volumetric flasks were heated to 80–90° during the development of the color, one might expect some hysteresis in their volumes. However, the volume change upon heating should be only 0.2% since the cubic coefficient of expansion of glass is about 0.0025% per degree centigrade, and any hysteresis should be smaller than this.

Standard 10-mm silica cells were employed; corrections for differences in path lengths were applied only in the differential measurements. All spectrophotometric measurements were made with a Beckman DU spectrophotometer at 654 nm.

Procedure

The complex was prepared by the procedure of AYRES AND YOUNG[16] but with the heating cycle shortened to 20 min because this appeared to yield slightly improved agreement with Beer's law at high absorbance values (Table I). An aliquot of the ruthenium solution was added to a 100-ml volumetric flask, and 15 ml of 0.2% (w/v) dithio-oxamide in glacial acetic acid (0.25 mmol) and 20 ml each of concentrated hydrochloric acid and ethanol were added. The flask and its contents were heated in a water bath at 80–90° for 20 min. A quantity of 1:1:2 hydrochloric acid:water: ethanol was then added and, after cooling to room temperature, the flask was filled to the meniscus with water. Blank solutions were prepared in an analogous fashion.

The reagents used in the preparation of the ruthenium standard solutions were shown to contribute about 0.00025 units to the measured absorbance.

Conventional measurements

As a test of Beer's law for this complex at high absorbance values, series of aliquots of three different ruthenium stock solutions were developed with dithio-oxamide and apparent molar absorptivities were calculated from the measured absorbance values. The average of these results (Table I) is $1.096 \cdot 10^4$ l/mole-cm with an estimated standard deviation of this mean of 0.40%. The amount of dithio-oxamide and the time of the color development have but slight if any effect on the molar absorptivity. For example, the average of those solutions for which the heating cycle was 20 min is $1.113 \cdot 10^4$ with a standard deviation of this mean of 0.35%.

TABLE I

APPARENT MOLAR ABSORPTIVITIES, $\varepsilon \cdot 10^4$ L/MOLE-CM, OF RUTHENIUM(III)–DITHIO-OXAMIDE COMPLEX AT 654 NM

(Bandpass 2 nm. Sensitivity intermediate. Color development at 80–90°)

Ru stock solution	*Color development (min)*	*Dithio-oxamide (mmol)*	*Nominal absorbance*							
			0.2	*0.4*	*0.6*	*0.8*	*1.1*	*1.3*	*1.7*	*2.2*
C_1	30–35	2.5	1.115	1.104	1.094	1.063	1.070			
C_1	45	2.5	1.098	1.079	1.074	1.072	1.033			
C_2	30–35	2.5	1.101	1.086	1.067	1.042	1.038			
C_2	20	2.5	1.128	1.125	1.117	1.118	1.110			
C_3	30–35	2.5	1.108	1.105	1.105	1.104	1.096			
C_3	20	5.0		1.111		1.110		1.105	1.107	1.083
C_3	20	5.0		1.131		1.132		1.113	1.105	1.104

This value of the molar absorptivity is only six-tenths of that reported by AYRES AND YOUNG[16] although it is in reasonable agreement with the value of $0.9 \cdot 10^4$ l/mole-cm which may be calculated from the Beer's law plot and sensitivity (0.011 μg Ru/cm^2) reported by XAVIER AND RAY[17]. JACOBS AND YOE[18] were also unable to achieve the sensitivity of AYRES AND YOUNG[16].

A molar absorptivity of $0.7 \cdot 10^4$ may be calculated from the data in Fig. 3 of ref. 19 (4 M hydrochloric acid, 80–85% ethanol). A molar absorptivity of about $5 \cdot 10^3$ may be calculated from the data of YAFFE AND VOIGT[20] but in a considerably different solvent ($[HClO_4] = 0.127\ M$, $[HOAc] = 50\%$, $\mu = 1.0$).

The ruthenium solutions used by AYRES AND YOUNG[16] were those employed in their study of the ruthenium–thiourea system[21] and were prepared by acidifying solutions of ruthenate with hydrochloric acid; the ruthenium content of these solutions was assayed gravimetrically and it is unlikely that these are in error. It is conceivable, however, that their solutions contained appreciable quantities of ruthenium(III) or monomeric ruthenium(IV) species and that this influenced the results. In a series of experiments designed to test these possibilities, a solution of ruthenium(III) was prepared by reducing solution C_2 with metallic mercury. (Spectrophotometric analysis of the initial and final solution after conversion to ruthenate indicated no change in the ruthenium concentration in this step.) The molar absorptivity for the dithio-oxamide complex obtained from aliquots of the reduced solution was $1.109 \cdot 10^4$ l/mole-cm. Molar absorptivities based on solutions prepared by dissolving solid $K_4RuCl_5ORuCl_5 \cdot H_2O$ and K_2RuCl_6 in 2 M hydrochloric acid were 1.14 and $1.08 \cdot 10^4$ l/mole-cm respectively. Thus the same degree of complex formation would appear to occur for standard solutions of monomeric ruthenium(IV), dimeric ruthenium(IV), or ruthenium(III).

A value of εb (b = path length) of $1.1 \cdot 10^4$ l/mole was used in the calculations for the differential measurements described below.

Differential measurements

In a differential measurement, the output of the photodetector of the spectrophotometer is balanced to 100% T with a reference (r) solution of known concentration in the light path. The absorbance of a sample (s) of unknown concentration will then be

$$A(C_r \text{ in } b_r,\ C_s \text{ in } b_s) = \varepsilon b_s C_s - \varepsilon b_r C_r + a(b_s - b_r) \qquad (1)$$

This equation is based on several assumptions:

(*a*) chemical equilibria, stray light and other factors which can cause deviations from Beer's law are not operative;

(*b*) reflection losses cancel completely;

(*c*) extraneous absorbing species are present in both solutions at the same concentration. This is the origin of the term $a(b_s - b_r)$.

In order to correct for differences in path length, a second measurement is needed in which the same solution is in both cells.

$$A(C_r \text{ in } b_r,\ C_r \text{ in } b_s) = \varepsilon b_s C_r - \varepsilon b_r C_r + a(b_s - b_r) \qquad (2)$$

Consequently,

$$C_s - C_r = \frac{A(C_r \text{ in } b_r,\ C_s \text{ in } b_s) - A(C_r \text{ in } b_r,\ C_r \text{ in } b_s)}{\varepsilon b_s} \qquad (3)$$

εb_s was taken to be $1.1 \cdot 10^4$ l/mole. A small error in this value introduces a negligible error into C_s because the maximum concentration difference between the solutions was less than 3%. Similarly, the values of $A(C_r \text{ in } b_r, C_r \text{ in } b_s)$ obtained with different solutions C_r should not vary by more than a few percent. Since this correction was typically only 0.1–0.2%, an averaged value was used throughout.

In principle, the concentration of the sample should be larger than that of the reference ($C_s > C_r$) in order to achieve maximum precision[22]. However, for the small concentration differences dealt with here, this criterion is not important. Consequently, all absorbances were measured both ways, sample *vs.* reference and reference *vs.* sample, and the values averaged.

RESULTS AND DISCUSSION

In order to estimate the accuracy with which standard solutions of ruthenium can be prepared by dissolving the metal in hypochlorite solutions, aliquots of seven ruthenium solutions prepared as described in the EXPERIMENTAL were developed with dithio-oxamide and the differences in concentration were determined spectrophotometrically. The results are presented in Table II and are summarized in Table III.

That the mean error for C_2-C_1 plus the mean error for C_3-C_2 equals the observed error for C_3-C_1 does not arise from the cancellation of terms. The measured differences among the other solutions are also consistent. Consequently, it seems reasonably certain that the results are independent of determinate errors.

For series 1A and 1B for which the absolute absorbances of the solutions are about one, the average squared mean error is 1.44/9 or about 0.16 $(\%)^2$. Since errors in the preparation of each standard solution contribute equally to this value, the variance of the individual solutions should be 0.16/2 or about 0.08 $(\%)^2$. Consequently, the standard deviation of the concentration of solutions of ruthenium prepared in this fashion is about 0.3%.

The data of series 2 indicate that the observed error increases when the spectrophotometric measurements are made at high reference absorbances. A 0.1% stray light component would explain this observation since for a concentration difference of 3%, 0.1% stray light should cause the measured concentration difference to be too small by 0.6% at a reference absorbance of 2.3, while the error introduced by stray light would be negligible for concentration differences below 1%. Such a value would be in line with Beckman's specifications for the stray light component for this instrument, 0.1% or less throughout the visible region, and would very neatly explain the apparent curvature of the Beer's law data in Table I at the higher absorbances. Direct measurement of the stray light with a didymium filter near 588 nm was attempted, but it was impossible to make such measurements with any precision at this small value of the stray light component.

The pooled estimate of the standard deviation of these measurements is 0.2% (75 degrees of freedom). This value is large in view of previous studies with the Beckman DU[6-11,14] and it would be even larger if all the results in Table II had been considered.

The overall variance of a differential spectrophotometric analysis is twice the instrumental variance (since two spectrophotometric measurements are needed for the application of eqn. (3)) plus the variance of the chemical steps. By instrumental variance is meant the reproducibility of all the steps after the formation of the colored complex: filling and positioning the cells, nulling the dark current and balancing

Table II. Differential Spectrophotometric Comparison Of Standards

Error = (Found - Theory)/C

Series No.	Theory, Micromolar	Error, %	Theory, Micromolar	Error, %	Theory, Micromolar	Error, %	Theory, Micromolar	Error, %	Theory, Micromolar	Error, %	Theory, Micromolar	Error, %
1A. C ∿ 0.0001 M, Bandpass ∿ 8 mμ.												
	C_2-C_1		C_3-C_1		C_3-C_2							
1302	0.67	-0.06	2.27	0.21	1.60	0.28						
1306	0.67	0.19	2.06	0.36	1.49	0.20						
1307	0.47	0.03	2.10	0.34	1.63	0.17						
1312	0.67	0.19	2.13	0.34	1.46	0.25						
1313	0.52	0.45	2.10	0.94	1.58	0.52						
1B. C ∿ 0.0001M, Bandpass ∿ 12 mμ.												
	C_4-C_6		C_4-C_5		C_4-C_7		C_6-C_5		C_6-C_7		C_7-C_5	
1376*	0.01	-1.37	2.72	-1.14	2.23	-1.80	2.71	0.17	2.32	-0.49	0.39	0.72
1379*	0.01	-0.68	2.72	-0.59	2.33	-1.56	2.71	0.11	2.32	-0.81	0.39	0.91
1381	0.35	-0.05	2.87	-0.43	2.44	-0.67	2.52	-0.34	2.09	-0.63	0.43	0.26
1383	0.26	-0.15	2.80	-0.34	2.17	-0.50	2.54	-0.13	1.91	-0.39	0.63	0.21
1385*	0.05	-0.82	2.86	-0.39	2.33	-1.23	2.81	-0.53	2.28	-0.47	0.53	-0.14
1387	0.05	-0.10	2.86	-0.34	2.33	-0.64	2.81	-0.18	2.28	-0.61	0.53	0.33
1389	0.05	-0.20	2.56	-0.39	2.25	-0.48	2.51	-0.60	2.20	-0.65	0.31	0.15
1390	----	----	----	----	2.23	-0.73	----	----	2.20	-0.97	0.29	0.40
1393	0.05	-0.34	2.56	-0.57	2.25	-0.61	2.51	-0.24	2.20	-0.28	0.31	0.11
1394	0.05	-0.20	2.56	-0.57	2.25	-0.61	2.51	-0.92	2.20	-0.53	0.31	-0.12
1395	----	----	2.74	-0.20	----	----	2.69	-0.51	----	----	0.49	0.56
C ∿ 0.0002 M, Bandpass ∿ 60 mμ.												
	C_4-C_6		C_4-C_5		C_4-C_7		C_6-C_5		C_6-C_7		C_7-C_5	
1349	0.15	-0.16	5.17	-1.33	4.52	-1.26	5.02	-1.17	4.37	-1.17	0.66	-0.04
1352*	0.15	-0.07	5.17	-1.25	4.52	-0.19	5.02	-1.20	4.37	-0.11	0.64	-1.09
1361	0.15	0.14	5.54	-0.84	4.55	-0.79	5.39	-0.70	4.40	-0.78	0.99	0.09
1363	----	----	----	----	4.18	-1.01	----	----	4.03	-0.81	1.36	0.17
1367	0.61	-0.22	5.92	-0.96	4.77	-0.95	5.22	-0.67	4.07	-0.69	1.15	-0.01
1368	----	----	----	----	4.93	-1.30	----	----	4.23	-0.85	0.99	0.37
1372	0.21	0.02	5.56	-0.79	4.59	-0.86	5.35	-0.78	4.38	-0.92	0.97	-0.14
1373	----	----	----	----	4.22	-0.81	----	----	4.01	-0.77	1.34	-0.05

* discarded

TABLE III

SUMMARY OF SPECTROPHOTOMETRIC COMPARISONS OF RUTHENIUM STOCK SOLUTIONS

Error = (Found–Theory)/C	*Theory, $M\cdot 10^6$*	*Mean Error*[a], %	*(Mean Error)*^{2}, (%)^2	*dof*
1. $C_1 \sim C_2 \sim C_3 \sim C_4 \sim C_5 \sim C_6 \sim C_7 \sim 0.0001\ M$				
A. Sensitivity intermediate. Bandpass 8 nm				
C_2–C_1	0.6	0.16 ± 0.19	0.0256	4
C_3–C_1	2.1	0.44 ± 0.29	0.1936	4
C_3–C_2	1.6	0.28 ± 0.14	0.0784	4
B. Sensitivity high. Bandpass 12 nm				
C_6–C_7	2.2	−0.58 ± 0.16	0.3364	6
C_7–C_5	0.4	0.24 ± 0.13	0.0576	7
C_4–C_7	2.3	−0.61 ± 0.07	0.3721	6
C_6–C_5	2.6	−0.42 ± 0.21	0.1764	6
C_4–C_6	0.1	−0.11 ± 0.15	0.0121	5
C_4–C_5	2.7	−0.43 ± 0.13	0.1849	6
			1.44	
2. $C_4 \sim C_5 \sim C_6 \sim C_7 \sim 0.0002\ M$				
Sensitivity high. Bandpass 60 nm				
C_6–C_7	4.2	−0.9 ± 0.11		6
C_7–C_5	1.0	0.11 ± 0.10		6
C_4–C_7	4.6	−1.0 ± 0.15		6
C_6–C_5	5.2	−0.8 ± 0.33		3
C_4–C_6	0.35	−0.13 ± 0.12		3
C_4–C_5	5.6	−1.0 ± 0.28		3

[a] The quoted uncertainty in the mean is taken at the 90% confidence level for the appropriate number of degrees of freedom.

the spectrophotometer, reading the scale, thermal equilibrium in the spectrometer, etc. Possible sources of error in the chemical steps include calibration errors in the volumetric glassware, irreproducibility in the complex formation reaction, and lack of thermal equilibrium when aliquots are taken for analysis.

The magnitude of the instrumental precision can be estimated as the precision of repetitive measurements of the difference in absorbance of pairs of cuvettes containing portions of the same ruthenium dithio-oxamide solution. These measurements were made originally in order to correct for path length differences among the cells (*cf.* eqn. 2). It should be emphasized that the data were obtained over a period of several weeks and that the cuvettes were emptied, refilled, and repositioned in the spectrophotometer between successive series. The pooled standard deviation of 60 such determinations (54 degrees of freedom) is 0.0013 absorbance measurements. From this the instrumentally limited precision of differential spectrophotometric analysis under the given conditions can be estimated as $\sqrt{2} \times 0.0013 = 0.0018$ absorbance units or something less than 0.1% if the absolute absorbance of the reference standard is in the vicinity of two or more.

To test the magnitude of chemical irreproducibility in the formation of the ruthenium dithio-oxamide complex, equal aliquots of the same ruthenium stock solution were worked up simultaneously and the absorbances of these pairs of solutions were compared as follows. Cuvettes 1 and 3 were filled with portions of

TABLE IV

SPECTROPHOTOMETRIC COMPARISON OF EQUAL ALIQUOTS OF SAME RUTHENIUM STOCK SOLUTION

Error = (Found–Theory)/C *Series No.*	*Theory, $M \cdot 10^6$*	*Mean Error*[a], %	*(Mean Error)*^{2}, *(%)*^{2}
A. $C_7 \sim 0.0002\ M$ *Sensitivity high. Bandpass 60 nm*			
1357	0.02	1.10 ± 0.03	1.210
1359	0.37	−0.08 ± 0.02	0.006
1366	0.16	−0.29 ± 0.09	0.084
1371	0.37	−0.09 ± 0.05	0.008
B. $C_4 \sim 0.0001\ M$ *Sensitivity high. Bandpass 12 nm*			
1378	0.02	−0.19 ± 0.04	0.036
1380	0.02	−0.19 ± 0.14	0.036
1382	0.21	−0.39 ± 0.11	0.152
1384	0.06	−0.38 ± 0.19	0.144
1386	0.04	−0.52 ± 0.02	0.270
1388	0.04	0.36 ± 0.05	0.130

[a] The quoted uncertainty in the mean is taken at the 90% confidence level for 3 degrees of freedom.

one solution and cuvettes 2 and 4 were filled with portions of the other solution. The absorbance of cuvette 1 was measured against that of cuvette 2, 1 *vs.* 4, 3 *vs.* 2, and 3 *vs.* 4. A difference in concentration was calculated from eqn. (3) for each of these four measurements; the averaged results appear in Table IV.

The relative agreement of these four values is another measure of the instrumentally limited standard deviation while their average is a measure of the overall precision of this method of analysis. The instrumental standard deviations for series A and B are 0.05% and 0.06%, estimated from the pooled variances of the data within each series. (In principle, the standard deviation for series B should be about double that for series A because of the lower absolute absorbance of the reference standard used in series B.) The overall variance was estimated as the average squared mean error, about 0.21(%)^2; on this basis, the overall standard deviation, which includes chemical and instrumental effects, is about 0.5%. Because the overall standard deviation is considerably larger than the instrumental standard deviation, unknown errors in the chemical steps appear to limit the precision of this method.

AYRES AND YOUNG[16], using a Beckman DU spectrophotometer, report a relative standard deviation of 0.8% for the conventional spectrophotometric analysis of a series of 47 replicate samples (T = 0.393). Since this is very close to the chemical irreproducibility found in this study, it is clear that differential spectrophotometric measurements using this ligand offer little gain in precision over conventional measurements.

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SUMMARY

The precision of a single spectrophotometric determination of ruthenium as the dithio-oxamide complex is shown to be about 0.5% and to be limited by chemical rather than instrumental irreproducibility. The molar absorptivity of this complex is $(1.11 \pm 0.02) \cdot 10^4$ l/mole-cm at 654 nm, considerably smaller than reported previously. It is shown that solutions of ruthenium for use as spectrophotometric standards may be prepared with a precision of about 0.3% by dissolving weighed portions of the pure metal powder in alkaline sodium hypochlorite at pH *ca.* 10, taking precautions to avoid the loss of RuO_4 during the dissolution.

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DIE PHOTOMETRISCHE BESTIMMUNG VON BLEISPUREN UNTER VERWENDUNG VON 7-[α-(*o*-CARBOMETHOXYANILINO)BENZYL]-8-HYDROXYCHINOLIN

GERHARD RÖBISCH

Institut für Anorganische Chemie der Pädagogischen Hochschule, Potsdam (Deutsche Demokratische Republik)

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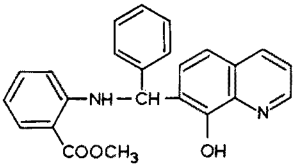
Keines der bisher bekannten photometrischen Reagenzien ist für Blei spezifisch oder auch nur hochselektiv. Blei muss deshalb vor seiner eigentlichen Bestimmung abgetrennt werden, wobei für die Photometrie insbesondere die extraktive Isolierung interessiert. Bei der Isolierung von Blei(II)-Ionen erfordert besondere Beachtung ihre Abtrennung von den sie hartnäckig begleitenden Wismut- und Thalliumionen. Als Extraktionsreagenzien für Blei besitzen Bedeutung das klassische Dithizon[1], das Natriumdiäthyldithiocarbamat (NaDDTC) (in Verbindung mit dem Diäthylammoniumdiäthyldithiocarbamat (DADDTC)[2,3]), mit geringerer Selektivität das N-Benzoyl-N-phenylhydroxylamin[4] und—trotz der Vorteile gegenüber dem NaDDTC praktisch noch wenig verbreitet—das Natriumdiäthyldithiophosphat[5]. Gut bekannt sind auch die verschiedenen Variationen der Extraktion des Tetrajodoplumbat(II)-Komplexes[6,7]. Besondere Vorzüge versprach nach UMLAND UND MECKENSTOCK[8] das bisher für die photometrische Bestimmung von Bleispuren noch nicht verwendete 7-[α-(*o*-carbomethoxyanilino)benzyl]-8-hydroxychinolin (CMAB-Oxin).

Blei gehört zu den Elementen, die sich mit 8-Hydroxychinolin (Oxin) nicht sehr gut extrahieren lassen. Blei(II)-Ionen bilden mit Oxin einen Komplex der Zusammensetzung $PbOx_2$, aber kein stabiles Dihydrat. Die Extraktion des Komplexes $PbOx_2$ gelingt wegen seiner geringen Stabilität nur bei relativ hoher Oxinkonzentration im pH-Bereich 9–12[9] bzw. 6–10[10]. Prinzipiell hochselektiv ist die extraktive Abtrennung von Blei unter Verwendung des 8-Hydroxychinaldin (2-Methyloxin) als Chelatbildner und Chloroform als Lösungsmittel[11,12]. In Anwesenheit von Cyanid und Wasserstoffperoxid werden lediglich Beryllium, Wismut und Blei extrahiert. Die Abtrennung gelingt aber nur von *kleinen* Mengen an Kationen und das Verhalten der in dieser Arbeit ebenfalls interessierenden Ionen In^{3+} und Tl^{+} (Tl^{3+}) war in die Untersuchungen nicht mit einbezogen. Die Störungen durch Wismut, Indium und Thallium (u.U. nach Aufoxydation zum Tl^{3+}) mussten aber vermeidbar sein bei Verwendung des CMAB-Oxins, das mit vielen Metall(II)-Ionen extrahierbare Komplexe bildet, jedoch, nach UMLAND UND MECKENSTOCK[8], bei Verteilung zwischen Wasser und Chloroform mit Metall(III)-Ionen nicht reagiert. Unter Beachtung der pH-Abhängigkeit der Extraktion der CMAB-Oxinate und in Gegenwart von Tartrat oder Citrat als Hilfskomplexbildner und Cyanid als Tarnreagenz soll die Extraktion von Pb^{2+}-Ionen spezifisch[8] sein.

VORUNTERSUCHUNGEN

CMAB-Oxin

Darstellung (nach PHILLIPS u.a.[13]): Je 0.2 mol Oxin, Anthranilsäuremethylester und Benzaldehyd werden in 200 ml Äthanol gelöst und bei Zimmertemperatur stehengelassen. Die Kristallisation beginnt nach 2 Tagen. Ausbeute nach 8 Tagen 55% d. Th. Nach Umkristallisieren aus Äthanol/Aceton (1:1) (auf 10 g Rohprodukt etwa 80 ml) weisse bis schwach gelbe, blättchenförmige Kristalle. Smp. = 133–134°. $C_{24}H_{20}O_3N_2$ (M = 384.44). Gut löslich in Chloroform, Benzol u.ä., löslich in Alkanolen, praktisch unlöslich in einer wässrigen Phase vom pH = 1–13.



Das Absorptionsspektrum des CMAB-Oxin, gelöst in Chloroform, zeigt die Abb. 1. Absorptionsmaxima treten auf bei 251 nm (ε = 93,200), 257 nm, 263 nm und 345 nm. Ab 400 nm, in dem Bereich, in dem die Absorptionsmaxima der CMAB-Oxinate liegen, absorbiert das Reagenz nur noch sehr schwach.

Messlicht

Das Absorptionsspektrum des Komplexes, den Blei(II)-Ionen mit dem

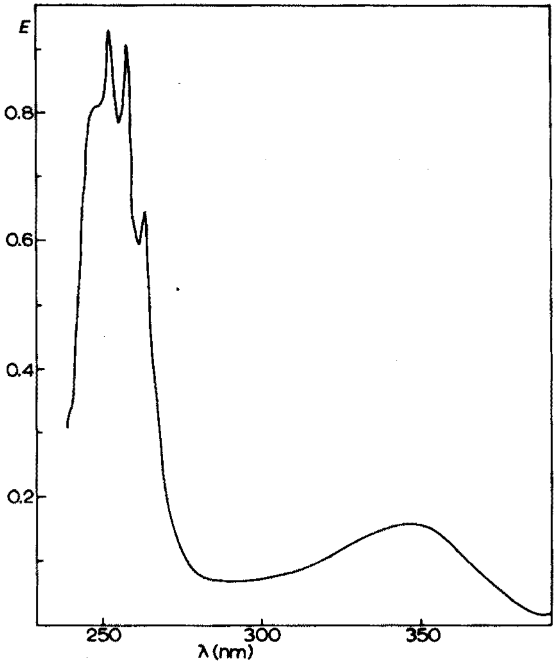


Abb. 1. Absorptionsspektrum einer 10^{-5} *M* Lösung vom CMAB-Oxin in Chloroform, gemessen gegen Chloroform, *d* = 1 cm. (Spectronic 505 der Fa. Bausch und Lomb, Rochester).

CMAB-Oxin bilden, gemessen gegen reine Reagenzlösung (in Chloroform), zeigt das Maximum bei 390 nm ($\varepsilon \approx 5000$) (Abb. 2). (Ein zweites, weit höheres Maximum liegt im UV bei 272 nm.) Die Messlösung wurde erhalten durch Schütteln einer wässrigen 0.051 mM $Pb(NO_3)_2$-Lösung, welche ausserdem 0.1 M an Citrat und 0.1 M an Cyanid war und den pH = 12.5 (Glykokollpuffer) hatte, mit dem gleichen Volumen einer 0.51 mM CMAB-Oxin-Lösung in Chloroform. Die Messung der Extinktion erfolgte bei einer Schichtdicke von 3 cm gegen reine Reagenzlösung (Kurve I).

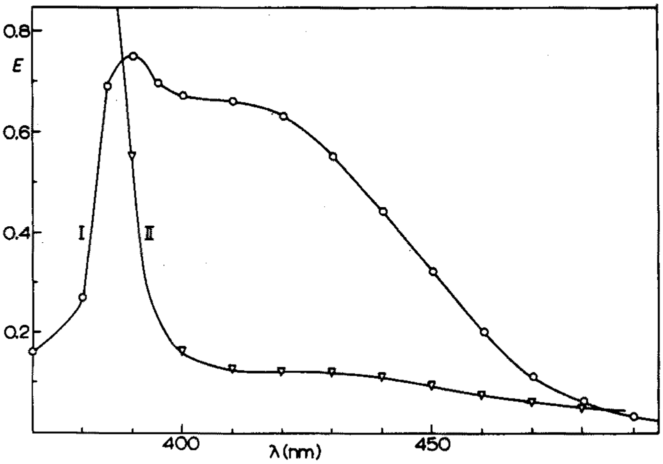


Abb. 2. Kurve I: Absorptionsspektrum einer Lösung des Pb-CMAB-Oxinats in Chloroform, gemessen gegen Reagenzlösung. Kurve II: CMAB-Oxin-Lösung in Chloroform gegen reines Lösungsmittel. $d = 3$ cm. (Spektralphotometer VSU des VEB Carl Zeiss, Jena).

Abbildung 2 zeigt ausserdem die Absorptionskurve der reinen Reagenzlösung, gemessen gegen Chloroform (Kurve II). Da die Eigenabsorption der CMAB-Oxin-Lösung bei dem Absorptionsmaximum des Blei-CMAB-Oxinats noch recht hoch ist, demnach mit einem sehr breiten Spalt gearbeitet werden müsste, wurde für die Messungen der Extinktion die Wellenlänge von 410 nm ($\varepsilon \approx 4500$) festgelegt.

Abhängigkeit der Extinktion vom pH der wässrigen Phase und von der Anwesenheit anderer Komplexbildner

Eine 0.24 mM $Pb(NO_3)_2$-Lösung, die ausserdem Cyanid (0.1 M) und Tartrat (0.1 M) oder Citrat (0.1 M) enthielt und deren pH durch Natronlauge- oder Salpetersäurezusatz potentiometrisch eingestellt war, wurde mit dem gleichen Volumen einer 2.4 mM Lösung von CMAB-Oxin in Chloroform geschüttelt. Die Messung der Extinktion erfolgte bei 410 nm gegen Reagenzlösung und bei einer Schichtdicke von 1 cm. Wie aus Abb. 3 ersichtlich, unterscheiden sich die Extraktionsbereiche bei Anwesenheit von Tartrat (Kurve I) und Citrat (Kurve II) um etwa eine pH-Einheit. Man erhält den Maximalwert der Extinktion bei Extraktion in Anwesenheit von Tartrat ab pH = 10, in Anwesenheit von Citrat ab pH = 11. Bis zum pH = 13 bleibt dann in beiden Fällen die Extinktion konstant. Eine sehr genaue Einstellung des pH-Wertes bei der Extraktion ist demnach nicht erforderlich. Die Cyanidionen haben keinen Einfluss auf die gemessene Extinktion, wie zusätzliche Versuche zeigten.

Abhängigkeit der Extinktion von der CMAB-Oxin-Konzentration

Die wässrige Phase, 0.24 mM Pb^{2+}, 0.1 M Tartrat, pH = 12.4 (Glykokollpuffer) wurde mit dem gleichen Volumen von CMAB-Oxin-Lösung in Chloroform (bei steigender Reagenzkonzentration) geschüttelt und dann die Extinktion der organischen Phase bei 410 nm, $d = 1$ cm, gegen reine Reagenzlösung gemessen. Es muss also wenigstens mit der achtfachen Reagenzmenge, bezogen auf Blei, gearbeitet werden. Weiterer Reagenzüberschuss, gemessen wurde bis zum hundertfachen, verändert die Extinktion nicht mehr.

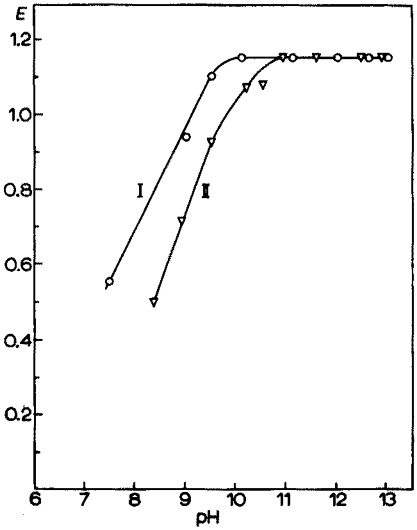


Abb. 3. Abhängigkeit der Extinktion einer Lösung des Pb-CMAB-Oxinats in Chloroform vom pH der wässrigen Phase. Kurve I: 0.1 M Cyanid, 0.1 M Tartrat. Kurve II: 0.1 M Cyanid, 0.1 M Citrat.

Schütteldauer und Lichteinfluss

Unter den im vorstehenden beschriebenen experimentellen Bedingungen genügen 3 Minuten Schüttelzeit zur Erzielung der maximalen Extinktion.

Beim Stehen der Messlösung im Sonnenlicht nimmt die Extinktion deutlich ab. Auch die Extinktion der Reagenzlösung verändert sich im Licht merklich schneller als im Dunkeln. Die Reagenzlösung wurde deshalb täglich frisch angesetzt und als Vorratsgefäss eine aussen mit schwarzem Papier beklebte Flasche verwendet. Die Messung der Extinktion der Messlösung erfolgte jeweils sofort nach der Phasentrennung.

DIE TESTUNG DES VERFAHRENS

Die Testung der extraktionsphotometrischen Bleibestimmung mit CMAB-Oxin wurde im wesentlichen nach der von GOTTSCHALK[14] angegebenen Methodik in zwei Arbeitsbereichen (Mikro I: 1.2–12 µmol Pb, Mikro II: 0.16–1.6 µmol Pb) vorgenommen.

Geräte

Spektralphotometer VSU 1 des VEB Carl Zeiss, Jena. pH-Meter OP 201/1 der Fa. Radelkis, Budapest, mit Einstab-Glaselektrode, Halbmikrokolbenbürette.

Reagenzien

Bleistandardlösung (Mikro I: 1.2 mM, Mikro II: 0.16 mM). Als Standardsubstanz diente $Pb(NO_3)_2$ p.a. (UCB), dessen Formelmasse durch 10 komplexometrische Bleibestimmungen (gegen Methylthymolblau)[15] zu 333.87 ± 0.15 ermittelt wurde. Entsprechende Einwaagen (auf der Halbmikrowaage) wurden in 1 l-Messkolben unter Zusatz von 5 Tropfen HNO_3 konz. in reichlich Aqua bidest. gelöst und unter Temperieren (20°) bis zur Marke aufgefüllt.

CMAB-Oxin-Lösung (Mikro I: 4.8 mM, Mikro II: 0.64 mM). Entsprechende Einwaagen an CMAB-Oxin löst man in den zugehörigen Volumina $CHCl_3$ p.a. (VEB Berlin Chemie). Chloroform wurde von uns besonders gereinigt und auch handelsüblich verwendet. Es traten keine Unterschiede auf. Die Lösung wird im Dunkeln aufbewahrt und täglich frisch angesetzt.

Pufferlösung. Glykokollpuffer nach Sörensen pH = 12.8. Kaliumcyanidlösung 1.25 *M*. Die verwendete KCN-Lösung war nie älter als 3 Tage.

Arbeitsbedingungen

In einem Schütteltrichter gibt man zu *a* ml ($a = 1, 2, 4, 6, 8, 10$) Bleistandardlösung, 2 ml 1.25 *M* Natriumcitratlösung, 5 ml Pufferlösung, 2 ml Cyanidlösung, und ergänzt mit Aqua bidest. auf 25 ml. Nach gutem Vermischen setzt man 25.00 ml CMAB-Oxinlösung zu und schüttelt 4 min. Nach der Phasentrennung wird die organische Phase durch ein trockenes Filter filtriert und in einer Küvette (Mikro I: $d = 0.5$ cm, Mikro II: $d = 3$ cm) die Extinktion bei 410 nm gegen Reagenzlösung gemessen.

ERGEBNISSE

Das Lambert–Beersche Gesetz ist in beiden Arbeitsbereichen streng erfüllt. Als praktischer Extinktionskoeffizient wurde der Wert $\varepsilon_{410} = 4.5 \cdot 10^3$ l mol^{-1} cm^{-1} gefunden.

Die Reproduzierbarkeit der Methode wird durch die aus jeweils 24 Messdaten erhaltenen Standardabweichungen s_K als sehr gut charakterisiert. Den Standardabweichungen entsprechen die in Tab. I angegebenen Variationskoeffizienten *V* (an der oberen (b_o) und unteren (b_u) Arbeitsbereichsgrenze) und die absoluten Fehlerbereiche *T* für die statistischen Sicherheiten *S*. Die unteren Bestimmungsgrenzen b_N wurden berechnet nach $b_N = \sqrt{2} \cdot |T\ 99.9|$:

Mikro I: 0.2 μmol Pb (in 25 ml); $E_N = 0.018$ ($d = 0.5$ cm)
Mikro II: 0.04 μmol Pb (in 25 ml); $E_N = 0.021$ ($d = 3$ cm)

Da in beiden Arbeitsbereichen das einfache Lineargesetz streng erfüllt ist, erfolgt die Berechnung der in der Probe gefundenen Bleimenge durch Multiplikation der aus der Testung erhaltenen Verfahrenskonstanten $[\omega]$ mit der gemessenen Extinktion *E*.

Mikro I: $[\omega] = 10.565$ μmol Pb
Mikro II: $[\omega] = 1.886$ μmol Pb

TABELLE I

FEHLERANGABEN FÜR DIE BLEIBESTIMMUNG

	Mikro I	*Mikro II*
s_K	± 0.029 µmol	± 0.007 µmol
V	±(0.24 bis 2.4) Rel-%	±(0.43 bis 4.3) Rel-%
T (S = 99%)	± 0.083 µmol	± 0.019 µmol
T (S = 99.9%)	± 0.112 µmol	± 0.026 µmol

Einfluss von Fremdionen

Die dieser Arbeit zugrundeliegende Aufgabenstellung, Bleispuren photometrisch in gesättigten, technischen Zinksulfatlösungen unterschiedlichen Reinigungsgrades zu bestimmen, führte zur Auswahl der im folgenden untersuchten Fremdionen. Die Fremdionen wurden als Lösungen ihrer p.a.-Salze zu Bleilösungen der unteren (b_u) und der oberen (b_o) Arbeitsbereichsgrenze zugesetzt und dann die Bleibestimmung durchgeführt. Das Fremdion stört, wenn das Ergebnis der Bleibestimmung ausserhalb des absoluten Fehlerbereiches T (S = 99%) liegt.

Keine Störung ergeben bis zu 1000 b_o: Alkalimetalle, Ca; bei erhöhtem Citratzusatz Al; bei erhöhtem Cyanidzusatz Cu, Zn, Cd, Co, Ni.

Magnesium wird unter den Bedingungen der Bleiextraktion (bei pH ~12.6) vollständig mitextrahiert. Der anwesenden Magnesiummenge entsprechend muss deshalb die CMAB-Oxin-Konzentration in der Chloroformphase u.U. erhöht werden. Das mitextrahierte Magnesium kann durch Schütteln der Chloroformphase mit einer Boratpufferlösung vom pH = 8 leicht abgetrennt werden. Das Blei bleibt unter diesen Bedingungen quantitativ in der organischen Phase. Nach erneuter Extraktion der Magnesiumionen mit CMAB-Oxin können diese sofort als Magnesium-CMAB-Oxinat sehr günstig photometrisch bestimmt werden[16].

Die Anwesenheit von Mangan(II) erfordert den Zusatz von Formaldoxim als weiterem Tarnreagenz[16]. Zur Herstellung der Formaldoximlösung gibt man zu 100 ml Aqua bidest., 10 g Paraformaldehyd und 22 g Hydroxylaminhydrochlorid. Unter Rühren erwärmt man, bis eine klare Lösung entsteht. Diese Lösung ist wenigstens eine Woche haltbar. In Abhängigkeit vom pH dieser Lösung enthält sie wechselnde Mengen der komplexaktiven trimeren Form des Formaldoxim[17]. Das Trimere des Formaldoxims bildet in alkalischer Lösung mit fast allen mehrwertigen Kationen gut wasserlösliche und z.T. farbige Komplexe[18]. Die zur Tarnung erforderliche Menge ist deshalb abhängig vom Gehalt an aktivem Reagenz in der Formaldoximlösung, der anwesenden Menge an Fremdkationen und der Konzentration an weiteren Komplexbildnern (Cyanid, Citrat).

Bei höherem Mangangehalt (>100 b_o) sind deshalb unter Berücksichtigung der konkreten Analysenproblematik Vorversuche zur Festlegung der zuzusetzenden Menge an Formaldoximlösung erforderlich.

Keine Störung ergeben bis zu 100 b_o Fe^{2+}; Fe^{3+} bei Anwesenheit von Formaldoxim. Grössere Eisenmengen werden günstiger durch Vorextraktion abgetrennt.

Bei Anwesenheit von Thallium muss Blei durch kurzes Schütteln mit einer Citratpufferlösung vom pH = 6 aus der chloroformischen in die wässrige Phase reextrahiert werden. Blei kann dann nach erneuter CMAB-Oxin-Extraktion bestimmt werden. (Diese Verfahrensweise ist auch in Anwesenheit anderer Fremdionen erfolgreich angewandt worden.)

Bei Anwesenheit von Indium ist die Citratkonzentration in der wässrigen Phase auf 1 M zu erhöhen, u.U. durch Zusatz von festen Citrat. Die Schütteldauer bei der Extraktion muss dann auf 20 min verlängert werden, wie überhaupt bei Erhöhung der Konzentrationen der verschiedenen Komplexbildner die Schüttelzeiten generell zu verlängern sind.

Wider Erwarten stört durch Mitbestimmung Wismut die Bleibestimmung empfindlich. Es lassen sich nur Wismutmengen von $< 1\ b_0$ tolerieren, wenn vor die eigentliche Bleibestimmung die oben beschriebene Reextraktion bei pH = 6 zwischengeschaltet wird. Es konnte aber kein pH-Wert gefunden werden, der eine Trennung grösserer Mengen der CMAB-Oxinate von Blei und Wismut durch Reextraktion des einen, gestattet. Möglich ist die Bleibestimmung in Anwesenheit grösserer Wismutmengen jedoch dann, wenn die Extraktion des Blei-CMAB-Oxinats in Anwesenheit einer hohen ($\geqq 1\ M$) Tartratkonzentration durchgeführt wird. Wismut wird dann vollständig maskiert, Blei unter diesen Bedingungen aber auch nicht mehr vollständig extrahiert. Die Extinktion sinkt um rund 25%. Die Methode dürfte deshalb nur in den Fällen erfolgreich anwendbar sein, in denen das in der Probe zu erwartende Verhältnis Pb : Bi einigermassen konstant ist und die Eichung unter entsprechenden Bedingungen durchgeführt wurde. Allgemein muss demnach Wismut durch Vorextraktion, z.B. mit DADDTC aus 6 N HCl[2], gesondert abgetrennt werden.

Schlussfolgerungen

Insgesamt erfordert die Abtrennung von Bleispuren und deren photometrische Bestimmung unter Verwendung von CMAB-Oxin einen geringen Arbeitsaufwand (damit ist verbunden insbesondere eine geringe Zahl an Fehlerquellen). Auch in der erzielbaren Selektivität ist die Methode (ausser dem Dithizon) den bisherigen photometrischen Blei-Bestimmungsmethoden überlegen. Die Empfindlichkeit lässt sich durch anreicherndes Extrahieren (das bei unserer Testung nicht berücksichtigt wurde) oder auch dadurch leicht erhöhen, dass die photometrische Bestimmung der Bleiionen nach ihrer Isolierung mit CMAB-Oxin und nachfolgender Reextraktion in der wässrigen Phase mit Pyridylazoresorcin (PAR)[7] vorgenommen wird.

Die völlig unerwartete starke Störung der getesteten Bleibestimmung durch das Wismut(III)-Ion war uns Anlass, Versuche über die Extrahierbarkeit einiger dreiwertiger Kationen mit CMAB-Oxin durchzuführen. Darüber wird gesondert berichtet.

Frau KARIN GOLDMANN danke ich für die gewissenhafte Durchführung der zahlreichen Versuche.

ZUSAMMENFASSUNG

Bleispuren lassen sich unter Verwendung von CMAB-Oxin hochselektiv und mit sehr guter Reproduzierbarkeit extraktionsphotometrisch bestimmen. Untersucht wurde der Einfluss von Al, Bi, Ca, Cd, Co, Cu, Fe, In, Mg, Mn, Na, Ni, Tl und Zn. Den bisher bekannten Eigenschaften des CMAB-Oxin widersprechend wird festgestellt, dass auch Wismut durch das Reagenz extrahiert wird und deshalb die Bleibestimmung stört.

SUMMARY

Traces of lead can be extracted and determined spectrophotometrically by means of CMAB-oxine. The molar absorptivity is $4.5 \cdot 10^3$ at 410 nm. The determination is highly selective in the presence of suitable masking agents; the influence of Al, Bi, Ca, Cd, Co, Cu, Fe, In, Mg, Mn, Na, Ni, Tl, Zn was examined. Bismuth is co-extracted by the reagent, but lead can be determined by a modified, less sensitive procedure.

RÉSUMÉ

Des traces de plomb peuvent être extraites à l'aide de CMAB-oxine /(7-α-(*o*-carbométhoxyanilino)-benzyl-hydroxy-8-quinoléine) et dosées spectrophotométriquement: Coefficient d'extinction molaire $4.5 \cdot 10^3$ à 410 nm. Ce dosage est très sélectif en présence d'agents masquants appropriés. On a examiné l'influence de Al, Bi, Ca, Cd, Co, Cu, Fe, In, Mg, Mn, Na, Ni, Tl et Zn. On constate que le bismuth est également extrait par ce réactif et gêne, par conséquent, le dosage du plomb.

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SHORT COMMUNICATIONS

Specific determination of americium with a recording spectrophotometer

The determination of americium has many features in common with the determination of plutonium. Both determinations can be done by radiochemical methods with their associated advantages and drawbacks, and for both elements spectrophotometric methods can be used.

For the spectrophotometric determination of americium(III) most authors[1,2] prefer to use the rather broad absorption band of this species at 812 nm instead of the stronger but sharp absorption band at 504 nm. It is to be expected, however, that measurement of the 504-nm peak, with application of the appropriate base-line technique and scale expansion as described already for the determination of plutonium(VI)[3], would lead to considerable improvement in the limit of detection and the selectivity. This communication describes the development of a procedure for the spectrophotometric determination of americium, based on an absorbance measurement at 504 nm.

Apparatus

The spectra were recorded with a Beckman DK-2A recording spectrophotometer, scale expansion being possible for the measurement of low absorbances. During the measurement the slit width can be read. For reasons of safety, the spectrophotometer was attached to a glove box as described elsewhere[3].

Selection of conditions

The trivalent state of americium is by far the most stable valency state in solution. In general, therefore, no special precautions have to be observed to ensure that no higher oxidation states are present. In cases of doubt, however, a small amount of hydroxylamine can be added to the solution. Absorbance measurements were made in hydrochloric and nitric acids of varying concentrations. Results are listed in Table I, from which it can be seen that the hydrochloric acid concentration has no effect on the absorbance, in contrast to the effect of varying nitric acid strength. Therefore, it was decided to use 3 *M* hydrochloric acid as a medium for the determination. This high acidity reduces the effects of potentially interfering anions of weak acids, such as phosphate, fluoride, etc.

The absorbances listed in Table I are independent of the slit widths used. All measurements can therefore be made with slit widths varying between 0.010 and 0.016 mm.

Interferences

The peak-absorbance value of the 504-nm americium band may be influenced by the presence of anions other than chloride. The values obtained in solutions

TABLE I

ABSORBANCES OF AMERICIUM(III) SOLUTIONS IN HYDROCHLORIC AND NITRIC ACIDS AT DIFFERENT SLIT WIDTHS (CELL LENGTH 1 cm)

160 mg of Am/l in HCl			*176 mg of Am/l in HNO_3*		
Acidity (M)	*Absorbance (E)*	*Slit width (mm)*	*Acidity (M)*	*Absorbance (E)*	*Slit width (mm)*
0.5	0.269	0.010	0.5	0.280	0.010
	0.266	0.011		0.283	0.010
	0.269	0.011		0.281	0.011
	0.269	0.016		0.280	0.015
1.0	0.268	0.010	1.0	0.258	0.010
	0.266	0.011		0.257	0.011
	0.267	0.011		0.260	0.011
	0.270	0.017		0.258	0.015
2.0	0.263	0.011	2.0	0.249	0.010
	0.266	0.012		0.245	0.010
	0.263	0.012		0.251	0.010
	0.265	0.016		0.247	0.015
4.0	0.269	0.010	4.0	0.217	0.011
	0.272	0.010		0.221	0.011
	0.271	0.011		0.219	0.012
	0.272	0.015		0.221	0.016

TABLE II

EFFECT OF ANIONS ON AMERICIUM DETERMINATION IN 3 *M* HYDROCHLORIC ACID

Anion	*Anion concn. (mmol/50 ml)*	*Am concn. (mg/50 ml)*	*Absorbance in presence of anion*	*Absorbance in absence of anion*
NO_3^-	10	0.65	0.216	0.219
	25	0.65	0.209	0.219
	50	0.98	0.291	0.329
F^-	10	0.65	0.217	0.219
	25	0.65	0.218	0.219
SCN^-[a]	25	0.69	0.260	0.233
$NH_2SO_3^-$	5	0.65	0.218	0.219
SO_4^{2-}	25	0.98	0.329	0.329
	50	0.98	0.323	0.329
$(COO)_2^{2-}$	10	0.69	0.229	0.233
PO_4^{3-}	25	0.98	0.341	0.329
	50	0.98	0.351	0.329

[a] Formation of sulphur due to decomposition of thiocyanate precludes precise measurement.

containing potentially interfering anions are listed in Table II. Interfering effects of all anions but thiocyanate are due to chemical interaction.

Cations generally interfere if their absorption spectrum obscures the position of the base line of the americium peak. The results of measurements of absorbances of americium in solutions containing various cations are listed in Table III.

For the study of the influence of plutonium in its different valency states, a few measurements were made in 4 *M* nitric acid (Table IV). The principle of the determination of americium in 4 *M* nitric acid is the same as in 3 *M* hydrochloric acid. Only the latter system is discussed in detail, however, as it was chosen for routine use for the reason already mentioned.

TABLE III

EFFECT OF CATIONS ON AMERICIUM DETERMINATION IN 3 *M* HYDROCHLORIC ACID

(The americium concentration was 0.65 mg/50 ml which gave an absorbance of 0.219 in the absence of other cations)

Cation	*Cation concn. (mg/50 ml)*	*Absorbance in presence of cation*	*Cation*	*Cation concn. (mg/50 ml)*	*Absorbance in presence of cation*
Mn^{2+}	1000	0.217	Fe^{3+}	100	0.211
Cu^{2+}	100	0.207	Ni^{2+}	100	0.213
Ce^{3+}	100	0.220	Ti^{4+}	100	0.220
	1000	0.220	UO_2^{2+}	25	0.214
Cr^{3+}	25	0.197		100	0.209
Rare earths[a]	—	0.228		1250	0.161
Fe^{2+}	100	0.216	NH_3OH^+	250	0.219

[a] Solution containing 20 mg of Nd^{3+}, 5 mg of Er^{3+} and 5 mg of Sm^{3+} per 50 ml.

TABLE IV

EFFECT OF CHLORIDE AND PLUTONIUM IONS ON AMERICIUM DETERMINATION IN 4 *M* NITRIC ACID

Cation or anion	*Concn. of foreign species*	*Am concn. (mg/50 ml)*	*Absorbance in presence of foreign species*	*Absorbance in absence of foreign species*
Cl^-	15 mmol/50 ml	0.84	0.219	0.219
Pu^{3+}	9 mg/50 ml	0.88	0.225	0.231
	25 mg/50 ml	0.88	0.244	0.231
Pu^{4+}	9 mg/50 ml	0.88	0.234	0.231
	25 mg/50 ml	0.88	0.243	0.231
PuO_2^{2+}	9 mg/50 ml	0.88	0.237	0.231
	25 mg/50 ml	0.88	0.223	0.231

The values reported in Tables II–IV are average values of duplicate measurements. For a more precise evaluation of interferences more measurements are required[4].

Recommended procedure

Transfer the sample containing 0.007–3 mg of americium to a 50-ml volumetric flask. If reducible substances are present, add 200 mg of hydroxylamine hydrochloride. Make up to volume in such a way that the final solution is 3 *M* in hydrochloric acid. Record the absorption spectrum of this solution from 450 to 550 nm in a 10-cm cell against 3 *M* hydrochloric acid as a blank. Take care that the slit width remains within the same limits as during the calibration measurements. Construct the base line on the recorded spectrum and measure the difference in absorbance between the peak maximum and the corresponding background. If scale expansion is used, convert the measured transmission value into absorbance before making the background correction. From the americium absorbance value thus obtained, determine the amount of americium from either a calibration line or an equation.

Calibration graph

A calibration graph was constructed according to the recommended procedure. For 0.010–3 mg of americium per 50 ml of final volume, the absorbances varied between 0.0030 and 1.010. The concentrations were verified by radiochemical measurements. From the results of 23 measurements, a least-squares calculation on the basis of a linear relationship $E = bC$, gave:

$$E = 0.3361\,C \tag{1}$$

where E is the measured absorbance in a 10-cm cell and C is the concentration in mg per 50 ml. No significant deviation from linearity could be detected. The molar absorptivity calculated from eqn. (1) amounts to 405.

Discussion

The precision of the method was determined by calculating the standard deviation, $s\{C_0\}$ of a concentration C_0, determined with the aid of eqn. (1) according to

$$s\{C_0\} = \frac{C_0}{E}\sqrt{s_E{}^2 + C_0{}^2 s_b{}^2} \tag{2}$$

where s_E is the standard deviation of an absorbance measurement, E the measured absorbance corresponding to C_0 and s_b is the standard deviation of b. For the whole concentration range the term $C_0{}^2 s_b{}^2$ was found to be small compared with $s_E{}^2$. The standard deviation can, therefore, be considered independent of concentration.

Because of the scale expansion used, the concentration range can be divided into two parts. For the lower concentration range (<0.2 mg/50 ml), a value of $s_E = 7.4 \cdot 10^{-4}$ was found, which leads to a standard deviation $s\{C_0\} = 0.0022$ mg/50 ml. In the higher concentration range (>0.2 mg/50 ml), the value $s_E = 3.9 \cdot 10^{-3}$ was found, which leads to $s\{C_0\} = 0.012$ mg/50 ml.

Since the method is a dependent one, its accuracy depends on the guaranteed purity of the sample used for calibration. Since no chemical standard for americium exists, analysis by α-counting was used in order to determine the concentration of the solutions used for calibration.

The limit of detection is defined[5] as $\partial C = 3.29\,C\,s_E/E$. In this equation the error of the second kind is accounted for. Substitution of the values for the lower concentration range gives $\partial C = 0.0072$ mg/50 ml. The scope of the method can thus be defined as 0.007–3 mg of americium per 50 ml.

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Euratom, European Institute for
Transuranium Elements,
Karlsruhe (Germany)

K. BUIJS
B. CHAVANE DE DALMASSY
M. J. MAURICE

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Substituted malonic acids as solvent extraction reagents

Virtually all the organic reagents used in solvent extraction processes act as singly charged ligands and the separation of cations depends on differences in the formation constants and distribution coefficients of the extracted species. Since only uncharged species are generally extracted into media of low dielectric constant the use of doubly charged ligands offers the possibility of introducing a new factor into solvent extraction separation processes. Knowledge of extraction by doubly charged ligands is at present sparse and appears to be restricted to some salicylate systems[1,2]. This communication is concerned with extraction by substituted malonic acids. Malonic acid itself forms uncharged mono-malonatocomplexes with divalent cations[3,4] but these are not extractable into organic solvents because of the hydrophilic nature of the species. However, it was envisaged that substitution at the methylene carbon atom might result in the formation of more hydrophobic species which would be more readily extractable and the extraction of cobalt(II) by a series of *n*-alkylmalonic acids has been examined to test this postulate.

In systems such as these where the uncharged chelate presumably retains coordinated water, the choice of solvent is of considerable importance. Such chelates are normally best extracted into oxygen-containing solvents and, accordingly, in the present work several such solvents have been investigated.

Reagents

The alkylmalonic acids were prepared by reacting sodium diethylmalonate with the appropriate alkyl bromide. The diethyl-*n*-alkylmalonates were separated from the reaction mixture by distillation and saponified to produce the *n*-alkylmalonic acids which were recrystallised from benzene. The acids prepared were *n*-octyl- (m.p. 112–3°), *n*-decyl- (m.p. 116–7°), *n*-dodecyl- (m.p. 118–9°) and *n*-hexadecyl- (m.p. 122–3°); the purity of the acids was checked by elemental analyses for carbon, hydrogen and oxygen and the results were within the accepted limits of accuracy.

Solvents were purified by the methods of PERRIN *et al.*[5]. Cobalt(II) was used as cobalt perchlorate.

Distribution experiments

The distribution of cobalt(II) was followed radiochemically by means of ^{60}Co. Equal phase volumes were shaken slowly to prevent emulsion formation. They were then separated by centrifugation and equal volumes of each phase were counted in a Baird Atomic Scintillation Counter. The percentage extraction was obtained directly from the count rates. For all the systems studied, shaking for 15 min was found to be sufficient to establish equilibrium. Prolonged shaking, particular at high pH, was found to produce lower extraction.

In the distribution experiments the total concentration of cobalt(II) was maintained at $2 \cdot 10^{-4}$ M, except in those specifically designed to investigate the dependence of distribution on cobalt(II) concentration.

Results and discussion

Table I lists the values of pH$_{\frac{1}{2}}$ and maximum percentage extraction for the extraction of cobalt(II) by 10^{-1} M *n*-dodecylmalonic acid in various solvents. In all of these systems, extraction fell sharply between pH 7 and 8. In addition to these solvents, di-isopropyl ether was also investigated, but a decrease in activity was observed in this system. In the 10^{-1} M *n*-dodecylmalonic acid–tributyl phosphate system, extraction was studied for different cobalt(II) concentrations within the range $2 \cdot 10^{-6}$ M–$2 \cdot 10^{-4}$ M. No significant variation was observed and it is concluded that the species extracted is monomeric.

TABLE I

EXTRACTION OF COBALT(II) BY DODECYLMALONIC ACID IN VARIOUS SOLVENTS

Solvent	$pH_{\frac{1}{2}}$	*Maximum extraction (%)*	*Dielectric constant*
Cyclohexanol	4.76	96.2	15
t-Amyl alcohol	4.80	94.3	5.8
n-Decanol	5.00	96.9	8.1
n-Octanol	5.20	96.5	10.3
n-Hexanol	5.55	96.6	13.3
2-Octanol	5.93	95.6	8.2
Methyl isobutyl ketone	6.05	96.0	13.1
Tributyl phosphate	6.36	94.8	8.0

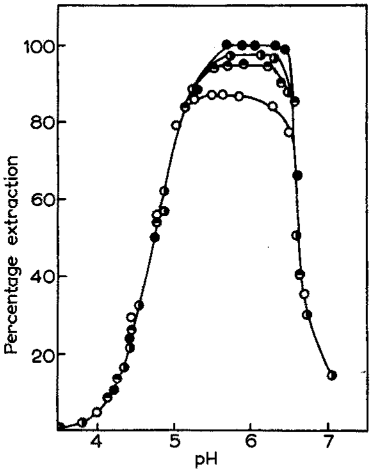

Fig. 1. Extraction of cobalt(II) by 10^{-1} M alkylmalonic acids in cyclohexanol. (○) *n*-Octylmalonic acid; (◓) *n*-decylmalonic acid; (◑) *n*-dodecylmalonic acid; (●) *n*-hexadecylmalonic acid.

Figure 1 shows pH profiles for the extraction of cobalt(II) by 10^{-1} M *n*-alkylmalonic acids in cyclohexanol. Similar sets of data were obtained for solutions of these acids in *t*-amyl alcohol and tributyl phosphate. These show that although the length of the alkyl group affects the maximum percentage extraction, it does not affect the value of pH$_{\frac{1}{2}}$ in a given solvent system. This type of behaviour is typical of solvent extraction systems involving closely-related ligands and has previously been observed with β-diketones, 8-hydroxyquinolines, dithizones and other ligands[6].

In the cyclohexanol system it can be seen that by using a longer alkyl group, *e.g.* dodecyl or hexadecyl, it is possible to obtain virtually quantitative extraction of cobalt(II). This same high percentage extraction is also obtained with dodecylmalonic acid in all the other solvents investigated, with the exception of di-isopropyl ether.

From the data in Table I it is possible to draw some preliminary conclusions about the effect of the solvent on these extraction systems. The first such conclusion is that the pH$_{1/2}$ is not dependent solely on the dielectric constants of the solvents although it must be admitted that the dielectric constants quoted are those of pure solvents not water-saturated solvents. Furthermore, while it can be seen that the oxygen function of the solvent has an effect on pH$_{1/2}$, it is also apparent that stereochemical factors have considerable influence on the pH region at which extraction occurs; *e.g.*, pH$_{1/2}$ for the cyclohexanol system differs by 0.79 pH units from pH$_{1/2}$ for the *n*-hexanol system, and there is a difference of 0.73 pH units between the pH$_{1/2}$ values of the *n*-octanol and 2-octanol systems. Further investigations are currently being made on the role of the solvent in these systems, and the solvent extraction studies are being extended to other cations.

Department of Chemistry,
University of Auckland,
Auckland (New Zealand)

J. AGGETT
M. H. TIMPERLEY

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Spot tests for mercapto compounds*

In order to prove the complete elimination of mercapto compounds by means of their reaction with alkali monochloroacetate[1], it was necessary to apply a sensitive test for thiols. Trials with sodium nitroprusside failed. The following new tests starting from alkaline solutions of the samples were found convenient; they may be carried out in spot test technique.

Tests based on the formation of mercury mercaptide

As has already been reported[2], mercury(II) cyanide remains unaltered towards 0.1 *N* sulfuric, phosphoric, nitric or oxalic acid, in contrast to alkali cyanides which immediately release hydrogen cyanide, which can be sensitively detected through the blueing of filter paper moistened with a solution of tetrabase and copper ethylacetoacetate in chloroform[3]. It is obvious that this behaviour not only permits the detec-

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* Dedicated to Prof. R. BELCHER on the occasion of his 60th birthday.

tion of alkali cyanides in the presence of mercury cyanide but also the detection of compounds which produce cyanide ions if treated with mercury(II) cyanide[4]. Acidic mercaptans and their water-soluble alkali salts belong in this category because of the reaction:

$$2\,RS^- + Hg(CN)_2 \rightarrow Hg(SR)_2 + 2\,CN^-$$

It is highly probable that thiophenols will behave like mercaptans.

The test for alkali-soluble mercapto compounds here described is specific provided that halogen ions are absent. It was found that hydrogen cyanide is also produced with compounds containing an acidic NH-group, such as saccharin, succinimide, phthalimide, etc.[5].

Procedure. In a micro test tube, a drop of alkaline test solution is placed followed by one drop of a 1% solution of mercury(II) cyanide. The mixture is then acidified by 0.1 *N* sulfuric acid. The tube is placed in a water-bath (80°–90°) and its mouth covered with a piece of filter paper moistened with the reagent. A blue fleck indicates a positive response.

Reagent for hydrogen cyanide. A solution containing 5% copper ethylacetoacetate and 5% tetrabase in chloroform.

Limits of identification. 2-Mercaptobenzothiazole 5 μg; 2-mercaptothiazoline 1 μg; 3,4,5,6-tetrahydro-2-pyrimidinethiol 2 μg; 2-mercapto-1-methylimidazole 5 μg; 2-mercaptoacetanilide 2 μg; mercaptosuccinic acid 5 μg; 4,6-diamino-2-mercaptopyrimidine 2 μg.

Another less sensitive test, likewise based on the rapid formation of white or yellow mercury(II) mercaptide makes use of the hitherto unknown fact that black mercury(II) sulfide is formed if the mercaptide is warmed with a sodium thiosulfate solution. We assume that the reaction is as follows:

$$Hg(SR)_2 + S_2O_3^{2-} \rightarrow HgS + SO_3^{2-} + RSSR$$

This assumption is supported by the behaviour of white or yellow lead or bismuth salts of thionalide and mercaptobenzothiazole towards thiosulfate. In all cases black sulfides are formed.

It may be noted that the above formation of sulfide also occurs on heating with powdered sulfur. The pertinent reaction $Pb(SR)_2 + S^0 \rightarrow PbS + RSSR$ is the basis of the so-called "Doctor test" widely used in the petroleum industry for the detection of mercaptans. CHERONIS AND ENTRIKIN[6] recommend this test for the detection of liquid mercaptans in mg amounts. The test here described, which can be regarded as a modified and improved Doctor test, is simpler and more sensitive.

Procedure. In a micro test tube, one drop of the alkaline solution of the sample is mixed with one drop of a 1% solution of mercury(II) cyanide and one drop of a 5% solution of sodium thiosulfate. The mixture is placed in a boiling water-bath for some minutes. A black precipitate indicates a positive response.

Limits of identification. Mercaptothiazoline 5 μg; 2-mercapto-1-methylimidazole 20 μg; 3,4,5,6-tetrahydro-2-pyrimidinethiol 25 μg; mercaptobenzothiazole 150 μg; 2-mercaptoacetanilide 2.5 μg.

Test based on the formation of copper(I) mercaptide

The water-insoluble copper(I) salts of mercapto compounds formed according to the reaction:

$$2\ RS^- + Cu_2^{2+} \rightarrow Cu_2(SR)_2$$

are yellow, orange yellow or orange brown. The reaction takes place at room temperature with the solid samples or with their solution in ammonia or caustic alkali.

Procedure. A drop of the test solution is treated with one drop of the reagent on a spot plate. If mercaptans are present, a yellow or brown precipitate or coloration results.

Reagents. (1) Copper(II) chloride (1.5 g) and 3 g of ammonium chloride are dissolved in a little water. The solution is treated with 3 ml of concentrated ammonia and made up to 50 ml with water.

(2) 20% Hydroxylamine hydrochloride solution in water. Equal volumes of (1) and (2) are mixed just before the test.

Limits of identification. Thioglycolic acid anilide (yellow) 2.5 μg; mercaptobenzothiazole (yellow) 5 μg; mercaptophenylthiadiazolone (yellow) 2.5 μg; potassium ethyl xanthate (yellow-brown) 1 μg; dithiooxamide (yellow-brown) 0.5 μg.

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Laboratorio da Produção Mineral,
Ministerio das Minas e Energia,
Rio de Janeiro (Brasil)

FRITZ FEIGL
DAVID GOLDSTEIN
ESTHER K. LIBERGOTT

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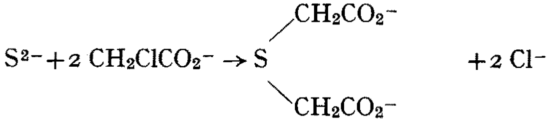
Note on the elimination of anions which contain reactive bivalent sulfur*

It is known from organic preparative investigations and the pertinent literature[1] that sulfur(II)-containing inorganic anions as well as anions of mercaptan compounds react with alkali monochloroacetate to form soluble thio compounds according to the reactions:



$$S^{2-} + 2\ CH_2ClCO_2^- \rightarrow S\begin{matrix} \diagup CH_2CO_2^- \\ \diagdown CH_2CO_2^- \end{matrix} + 2\ Cl^-$$

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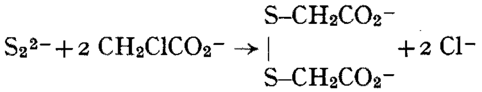
* Dedicated to Prof. R. BELCHER on the occasion of his 60th birthday.



$$S_2^{2-} + 2\,CH_2ClCO_2^- \rightarrow \begin{array}{l} S\text{–}CH_2CO_2^- \\ | \\ S\text{–}CH_2CO_2^- \end{array} + 2\,Cl^-$$

$$S_2O_3^{2-} + CH_2ClCO_2^- \rightarrow {}^-O_3S\text{–}S\text{–}CH_2CO_2^- + Cl^-$$

$$CNS^- + CH_2ClCO_2^- \rightarrow {}^-SCN\text{–}CH_2CO_2^- + Cl^-$$

$$RS^- + CH_2ClCO_2^- \rightarrow RS\text{–}CH_2CO_2^- + Cl^-$$

We have tried to develop a test for the above sulfur(II)-containing ions through the detection of chloride ions formed by the respective reactions with monochloroacetate. No characteristic results were obtained because chloride-free preparations of monochloroacetate were not available. In compensation, another analytical application was achieved through the finding that the above condensations rapidly lead to the complete elimination of S^{2-}, $S_2O_3^{2-}$, etc. ions in alkaline media. This is illustrated by the following experiments carried out by spot test technique.

A drop of the 1% test solution was placed in a micro test tube together with some grains of sodium monochloroacetate or with some drops of an ammonical solution of the ammonium salt prepared by addition of excess of ammonia to monochloroacetic acid. The mixture was warmed (water bath) for 5 min and then tested for:

1. S^{2-} ions by reactions with sodium nitroprusside, lead acetate or plumbite;
2. $S_2O_3^{2-}$ ions by reaction with diluted mineral acid;
3. SCN^- ions by reaction with an acidic solution of iron(III) chloride;
4. RS^- ions by reaction with copper(I)[2].

In all cases the responses to these delicate tests were negative. It may be noted that the elimination of mercaptan compounds was proved with 12 pertinent thiols.

In accordance with the elimination of sulfide ions by means of monochloroacetate are the following observations*. Freshly prepared MnS, ZnS, Tl_2S and UO_2S are dissolved when warmed with a solution of alkali monochloroacetate, in contrast to other basic sulfides with a smaller solubility product, which remain unaltered. Furthermore, neutral solutions of Mn, Zn, Tl(I) and UO_2 salts which contain excess of monochloroacetate remain unaltered if some drops of diluted alkali sulfide are added.

An interesting application of the elimination of sulfide ions was found in the behaviour of solutions of As_2S_3 in ammonia or caustic alkali which contain the equilibria:

$$AsSO_2^{3-} + 2\,OH^- \rightleftarrows AsO_3^{3-} + S^{2-} + H_2O$$

$$AsS_2O^{3-} + 4\,OH^- \rightleftarrows AsO_3^{3-} + 2\,S^{2-} + 2\,H_2O$$

The addition of monochloroacetate and short warming destroys the equilibria and leads to the quantitative formation of arsenite ions. CALDAS[3] has recently recommended this conversion and the similar conversion of antimony and tin sulfosalts for the detection of acidic sulfides in the scheme of qualitative inorganic analysis.

Water-soluble organic compounds which are sulfide donors due to hydrolysis likewise react with monochloroacetate and may be eliminated in this way. Pertinent

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* Communication from E. JUNGREIS, Hebrew University (Jerusalem).

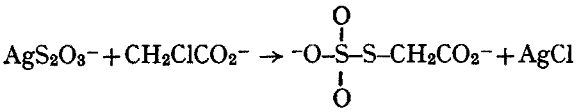
compounds are thioacetamide, which is widely used in inorganic analysis[4], other thioamides, *e.g.* dithiooxamide (rubeanic acid), and alkali salts of thiocarboxylic acids. The same is true with thiourea which may react in alkaline media in its tautomeric iso form like mercapto compounds.

The behaviour of alkali sulfites deserves attention. If a diluted solution of alkali sulfite is warmed with an excess of monochloroacetate and then acidified, sulfur dioxide is released. This permits the detection of sulfite in mixtures with sulfide and thiosulfate ions.

The elimination of thiosulfate ions by means of monochloroacetate ions may be applied for the detection of silver halides dissolved in alkali thiosulfate. This problem is of interest in photography in order to eliminate silver halides. The initial reaction

$$AgX + Na_2S_2O_3 \rightarrow AgNaS_2O_3 + NaX \text{ (where X = halide)}$$

is followed by the addition of sodium thiosulfate to form water-soluble $Na_5\{Ag(S_2O_3)_3\}$[5]. We have found that the addition of monochloroacetate to silver thiosulfate compounds leads to the precipitation of silver chloride according to



$$AgS_2O_3^- + CH_2ClCO_2^- \rightarrow {}^-O\text{–}\overset{\overset{\text{O}}{|}}{\underset{\underset{\text{O}}{|}}{\text{S}}}\text{–S–}CH_2CO_2^- + AgCl$$

If this reaction is carried out in the presence of excess of alkali iodide, silver iodide is produced.

The reaction of complex silver thiosulfate with monochloroacetate can be considered as demasking, monochloroacetate acting as the demasking agent. It may be expected that other complex thiosulfates will behave like the silver complex with respect to this demasking.

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Laboratorio da Produção Mineral,
Ministerio das Minas e Energia,
Rio de Janeiro (Brasil)

F. FEIGL
A. CALDAS

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Minimization of phosphorescence background with commercial cells in phosphorimetry

Qualitative measurements of phosphorescence at low concentrations of organic phosphors have in the past been plagued by two errors[1]: the poor reproducibility of sample tube alignment; and variable phosphorescence background from pickup of phosphorescent impurities in the sample tube. The first error has been minimized by means of the rotating sample tube method of HOLLIFIELD AND WINEFORDNER[2]. The second error, which has been more difficult to reduce, is minimized by the clean-up procedure discussed in this note. Variable phosphorescence background results in increased detection limits and poorer precision at higher concentrations. The background contamination is primarily a result of two sources: sample transfer and contaminated glassware.

Because sample tubes are long and narrow with a large internal surface area, they are difficult to clean and fill with sample. When the sample tube is filled with a solution differing from the one in the tube, minimal phosphorescence background from the previous sample and pickup of phosphorescence impurities results if the sample tube is rinsed three times with new sample, and after each rinse, the sample tube with solution is placed in an *ultrasonic cleaner* for about 30 sec. Introduction and removal of the sample into and from the sample tube is best accomplished by means of a syringe with a blunted needle which reaches to the bottom of the sample tube. Aspirator systems in which polyethylene tubing is used result in contamination from leaching of plasticizers by many solvents. Any trace of fingerprints remaining on the outside of the sample tube are removed by using a new Kim-Wipe tissue each time the tube is used.

The cleanliness of all glassware to be used in preparation of samples and/or standards is also extremely important. The glassware to be used is placed in a concentrated nitric acid bath at ambient temperature for 24 h and then rinsed five times with tap water and three times with redistilled water (free of organics, *e.g.*, organics used to retard growth of microorganism) and oven-dried (free of organic materials which may char causing a background). On the other hand, glassware can be cleaned in an ultrasonic cleaner for 3 to 4 h instead of the nitric acid bath and then rinsed as described above.

Pipettes used to prepare samples and standards should be cleaned in an automatic pipette washer; the pipettes are soaked in laboratory glass cleaner, rinsed for 12 h with tap water, rinsed several times with redistilled water, and finally oven-dried.

Some contaminants are unusually strongly adsorbed to the quartz sample tube but can be removed by heating in a flame to a red glow. This treatment will remove those compounds which phosphoresce strongly and are resistant to nitration, *e.g.*, retene.

Finally each sample tube should be checked for any intrinsic phosphorescence because some have substantial quartz background.

As can be seen from the data in Table I, there is considerable improvement in the signal-to-background fluctuation (reproducibility) when the new clean-up procedure is used for ethanol (excitation at 262 nm and emission at 380 nm) rather than the conventional procedure. It should also be noted that the signal-to-noise ratio with

TABLE I

COMPARISON OF SIGNALS AND SIGNAL-TO-NOISE RATIOS WITH ROTATING SAMPLE CELL AND WITH OR WITHOUT NEW CLEAN-UP PROCEDURE

	Signal (nA)[a,b]	*Signal-to-background fluctuation*[b,c]	*Signal-to-noise*[b,d]
Conventional clean-up procedure	~ 1.5 (0.05)[e,f]	~ 2.5	~ 100 (15)[e]
New clean-up procedure	~ 0.3[f]	~ 25	~ 45

[a] Signal is due to impurities in ethanol (solvent) background.
[b] All signals, signal-to-background fluctuations, and signal-to-noise ratio are approximate. Excitation is at 262 nm and emission is measured at 380 nm.
[c] Background fluctuation is standard deviation of five background readings.
[d] Time constant for all measurements was 0.3 sec.
[e] Values in parentheses were obtained without the Aminco elliptical condensing system (American Instrument Co., Inc., Silver Springs, Md.).
[f] Dark current is ~ 0.02 nA.

either clean-up procedure obeys a square-root relationship as would be expected from a shot-limited noise[3]. Also the signal-to-background fluctuation and signal-to-noise are independent of wavelength. When the rotating sample cell and the new clean-up procedure are used, the background fluctuation is of the same order of magnitude as the peak-to-peak noise on the phosphorescence background. Therefore, with the above clean-up procedure, the limits of detection can be lowered by about one-hundred-fold compared to those listed by WINEFORDNER *et al.*[1]. The one-hundred-fold improvement is a result of a ten-fold improvement due to the use of the rotating sample cell[1] compared to the conventional stationary sample cell, and the other ten-fold improvement is due to the use of the new clean-up procedure rather than the conventional procedure.

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Department of Chemistry,
University of Florida,
Gainesville, Fla. 32601 (U.S.A.)

RUTH ZWEIDINGER
LOWELL B. SANDERS
J. D. WINEFORDNER

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Determination of trace elements in seawater by neutron activation analysis

Trace elements in seawater (those in concentrations of parts per billion to subparts per billion) have been measured in the past by a variety of techniques, *e.g.* atomic absorption spectrophotometry, neutron activation analysis, colorimetry, and isotope dilution. All these methods have a common disadvantage: it is necessary to perform a rather sophisticated chemical separation and enrichment of the elements of interest before analysis. Systematic errors introduced by contamination or partial loss of an element during this step of the analysis are often difficult to evaluate. The present paper describes a method of neutron activation analysis whereby the abundances of several trace elements can be determined directly and simultaneously in the dried sea salt.

Samples analyzed consisted of filtered and unfiltered water and suspended matter, as determined by filtration through a 0.45-μ filter. They were collected from Framvaren, an anoxic fjord in the district of Lista, Norway[1].

Experimental

Seawater (100 ml) was freeze-dried on the walls of a 1-l polyethylene bottle. The salt was then packaged in a quartz vial. Each sample of suspended matter, along with the filter used to collect the material, was similarly sealed in a quartz vial. The vials were placed in aluminum cans, three per can, together with a flux monitor. The monitors represented single splits of a mixture of preweighed amounts of Co, Cr, Cs, Fe, Rb, Sb, Sc, Sr, and Zn. Zirconium and lanthanum, which also may be determined by this technique, were not added to the monitors, owing to failure to anticipate this opportunity.

Samples and monitors were irradiated in the CP-5 reactor at Argonne National Laboratory. They were later transferred to polyethylene vials and the γ-ray spectra were measured (Fig. 1) with a 30-cm^3 Ge(Li) detector and a 1024-channel analyzer[2]. An irradiation time of one week and a counting time of 1000 min was considered necessary to attain the desired sensitivity. The large amount of ^{24}Na (half-life 15.0 h) and ^{82}Br (half-life 35.3 h) produced imposed a 4- to 5-week cooling period between the irradiation and counting.

Results and discussion

Abundances of elements can be calculated from the γ-ray spectral data in one of two ways: (*a*) activities of elements in the sample are compared with corresponding activities in the external flux monitor irradiated in the same aluminum can; (*b*) some element in the sample, in this case strontium, is used as an internal flux monitor[3]. The assumptions that must be made in using the latter method are (1) that strontium is conservative, and (2) that the ratio of the specific activities of strontium to each of the elements is the same in all samples and monitors. To determine the validity of the first assumption, strontium was determined independently by atomic absorption spectrophotometry in 10 samples. When normalized to 19$^0/_{00}$ chlorinity, its concentration in all 10 samples was 7.8 ± 2 p.p.m., in agreement with values reported for oceanic water[4-6]. All samples were irradiated in the most highly thermalized flux available in the reactor, with a ratio of thermal to fast neutrons[7] of approximately 10^{13} n cm^{-2}

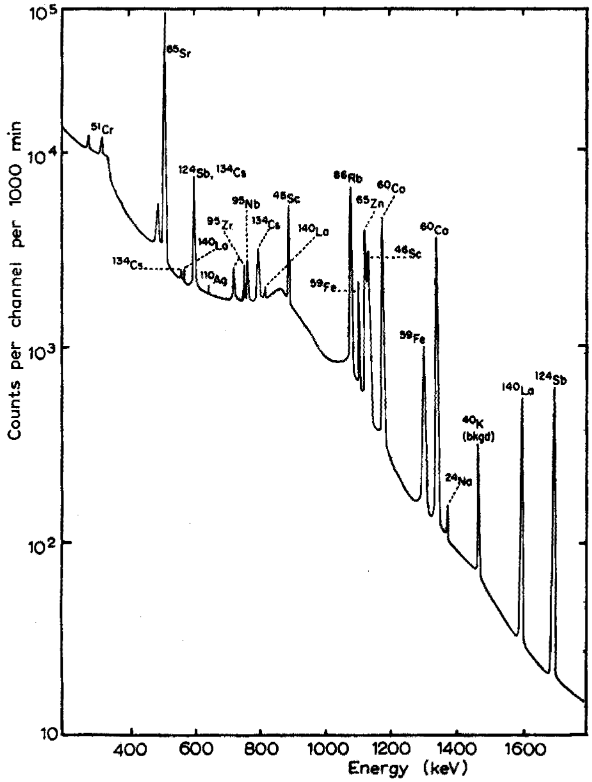

Fig. 1. Spectrum of γ-rays from a sample of freeze-dried sea salt observed with a 30-cm^3 Ge(Li) detector, 32 days after irradiation.

TABLE I

ELEMENTAL ANALYSIS OF FOUR 100-ml ALIQUOTS OF A SINGLE WATER SAMPLE

(Three of the samples were spiked with cobalt, chromium, and iron. All measurements are in μg/100 ml)

Element	*Untreated*	*5 μg spike*	*10 μg spike*	*15 μg spike*
Co	0.044	4.9	10.	14.
Cr	0.048	4.8	10.	15.
Fe	2.3	7.0	12.	17.
Element	*Untreated*			
Sr				
Rb	10.5	10.1	10.3	10.4
Cs	0.022	0.021	0.022	0.024
Sc (10^4)	0.63	0.59	0.51	0.59
Sb	0.059	0.063	0.58	0.57
Zn	1.3	—	—	—

sec^{-1}: 10^{10} n cm^{-2} sec^{-1}, thus minimizing variations in the ratios of specific activities. The success in minimizing these variations was indicated by determining the abundances of cobalt, chromium and iron in three aliquots of a single sample spiked with known amounts of each (Table I).

The advantages of using an internal flux monitor are as follows. No errors result from slight differences in geometry between samples and monitors in the reactor and in the counting chamber. Errors resulting from differences in shadowing between monitors and samples are eliminated. Attenuation of neutrons, mostly by ^{35}Cl, was estimated to have caused specific activities to be as much as 14% lower in samples than in the external flux monitors. Abundances are calculated by comparing activity ratios of strontium and each of the other elements in the sample with the average of the corresponding ratios for all monitors, thus minimizing mixing, splitting, and weighing errors of monitors. These errors account for standard deviations of about 10% in activity ratios of monitors. Activity ratios of strontium to the other conservative elements in the seawater, cesium and rubidium, exhibited standard deviations of only 4%, less than half those observed in the monitors.

The percentages of variation, determined by analyzing four aliquots of a single sample, are Rb 4%, Cs 10%, Sc 20%, Sb 10%, Fe 12%, Co 4%, and Cr 8%. Precisions for chromium and cobalt represent lower limits since they are approximately two orders of magnitude more abundant in the spiked samples, used for these calculations, than in seawater. The concentration of zinc cannot be determined in samples spiked with cobalt, because of the interference between the zinc peak and the Compton edge associated with the 1332-keV cobalt peak.

Abundances of elements in suspended matter were calculated by the same method after corrections were made for the presence of the elements in the filters (Table II).

The measurements of Co, Cr, and Fe in the three spiked samples (Table I) give an estimate of the accuracy of the technique. Possibly the most important factor

TABLE II

ABUNDANCES OF TRACE ELEMENTS IN A MILLIPORE FILTER AND IN THE SUSPENDED MATTER COLLECTED BY FILTERING 45 l OF SEAWATER

(Abundances are in μg)

	Sr	*Rb*	*Cs*	*Sc*	*Co*	*Sb*	*Zn*	*Cr*	*Fe*
Filter	12	—	—	—	—	1.9	5.8	11	10
Seawater	0–2	—	—	0.015–0.06	0.4–0.19	—	2–16	1–14	225–1000

TABLE III

CONCENTRATIONS OF ELEMENTS IN SUSPENDED MATTER, MEASURED DIRECTLY AND DETERMINED BY CONSIDERING THE DIFFERENCES IN THEIR CONCENTRATIONS IN FILTERED AND UNFILTERED WATER SAMPLES

Depth (m)	*Suspended matter*					
	Measured (μg/l)			*Calcd. by difference (μg/l)*		
	Co	*Cr*	*Fe*	*Co*	*Cr*	*Fe*
1	0.008	0.26	4.8	—	0.36	5.0
20	0.041	0.18	13	0.036	0.33	15
55	0.014	—	13	0.010	—	13

affecting accuracy is contamination of the samples during storage. Polyethylene bottles, used to store the water samples, may contain relatively large abundances of several of the elements measured[8]. To minimize contamination, the bottles were filled with 1 *N* nitric acid for 2 weeks, and fjord water for 1 week, before collection of the samples. Contamination was estimated to be relatively small by comparing the concentrations of elements in suspended matter measured directly with those calculated by taking the differences in concentrations in filtered and unfiltered water samples (Table III).

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Scripps Institution of Oceanography,
La Jolla, Calif. (U.S.A.)
University of California, San Diego,
La Jolla, Calif. (U.S.A.)

DAVID Z. PIPER*
GORDON G. GOLES**

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* Present address: Department of Oceanography, University of Washington, Seattle, Wash. 98105.

** Present address: Departments of Chemistry and Geology and Center for Volcanology, University of Oregon, Eugene, Oreg. 97403.

The determination of iron by atomic fluorescence spectroscopy with a modulated microwave-excited electrodeless discharge tube

Recent studies[1–5] on atomic fluorescence spectroscopy (a.f.s.) have recognized the importance of source intensity in a.f.s., and the use of microwave-excited electrodeless discharge tube sources has been recommended[6–8]. The atomic fluorescence of iron at 248.3 nm in air–hydrogen and air–propane flames with a 150-W xenon arc continuous source has been reported[4], a detection limit of 5 p.p.m. being obtained in both flames. WINEFORDNER *et al.*[9] report a detection limit of 0.25 p.p.m. for iron fluorescence at 248.3 nm in an air–hydrogen flame with an electrodeless discharge tube as source. MARSHALL AND WEST[10] have described the application of an iron microwave-excited electrodeless discharge tube to the determination of iron by atomic absorption spectroscopy. This paper reports the results of a study of the analytical application of a.f.s. to the determination of traces of iron. The optimum conditions for the determination of iron in an air–acetylene flame with a commercial flame spectrophotometer have been established. The preparation and properties of iron microwave-excited electrodeless discharge tubes have been studied, and the sensitive and selective determination of microgram amounts of iron by a.f.s. with these sources is described.

Apparatus

A Unicam SP 900A flame spectrophotometer (Unicam Instruments Ltd., Cambridge) modified for a.f.s. as described elsewhere[4], was used. The circular stainless steel Meker-type burner and indirect cyclone nebuliser unit of this instrument were employed without modification. The nebuliser spray rate was 3 ml/min when the air pressure to the flame *via* the nebuliser unit was maintained at 28 p.s.i. An EMI 9601B photomultiplier was fitted in place of the standard EMI 9529B to obtain higher sensitivity in the ultraviolet region.

The iron electrodeless discharge tube was operated at 2450 MHz with a 200-W Microtron 200 Mark II power generator and ¾-wave Broida-type resonant cavity (Electromedical Supplies Ltd., London, Type 210L). The tube output was modulated at 50 Hz. For this purpose the phasing coils of the SP 900A absorption chopper unit were disconnected, and the flame spectrophotometer amplifier was triggered by the synchronisation output from the modulator unit. The SP 900A was then operated in its "absorption" mode. The burner unit was placed 50 mm in front of the monochromator entrance slit, so that the slit viewed the flame between 2 and 22 mm above the primary reaction zone. The source was positioned at 90° to the burner–monochromator axis and in the same horizontal plane, so that the distance between the electrodeless discharge tube and the centre of the flame was 50 mm. The use of a focussing lens between the source and the flame did not appreciably improve the sensitivity.

Preparation and operation of electrodeless discharge tube

The preparation of iron electrodeless discharge tubes from the element and iodine[10], the element and chlorine[11], iron(II) chloride[8] and iron(II) iodide with iron[9] has previously been reported. Each of these methods of preparation was examined in this study in an attempt to produce the most stable and intense tubes which had extended operating life-times. The tubes were prepared by the general procedure described elsewhere[11]. The most satisfactory results were obtained for tubes containing *ca.* 15 mg of iron(II) chloride with an argon filler with gas pressure of 3 mm of mercury. Hydrated iron(II) chloride was dehydrated *in situ* in the tube by repetitive heating at reduced pressure before the tube was sealed.

The iron tubes were operated in the ¾-wave resonant cavity at 60 W with air cooling to the length of the tube. After an initial "running-in" for between one and two hours, only 5 minutes "warm-up" period was required after initiation of the discharge. With these operating conditions, the line-to-background ratio at 248.3 nm was typically greater than 100:1, while the short term output stability of the radiation at this wavelength was ±3% over a period of several hours. The discharge obtained exhibits

TABLE I

RELATIVE SOURCE AND FLUORESCENCE INTENSITIES AND DETECTION LIMITS

Wavelength (nm)	*Transition (ref. 12, 13)*[a]	*Relative intensities from source*[b,d]	*Relative fluorescence intensities*[b,d]	*Limit of detection for iron (p.p.m.)*
386.0	$a^5D_4 - z^5D_4^0$	50	23	15
382.0[c]	$a^5F_5 - y^5D_4^0$	127	193	1.2
382.4[c]	$a^5D_4 - z^5D_3^0$			
382.6[c]	$a^5F_4 - y^5D_3^0$			
372.0	$a^5D_4 - z^5F_5^0$	135	328	0.84
356.5[c]	$a^5F_3 - z^3G_4^0$	8	54	4.2
357.0[c]	$a^5F_4 - y^5D_3^0$			
302.1[c]	$a^5D_3 - y^5D_3^0$	24	85	6.0
302.06[c]	$a^5D_4 - y^5D_4^0$			
302.05[c]	$a^5D_2 - y^5D_2^0$			
298.4	$a^5D_4 - y^5D_3^0$	23	70	3.6
272.1[c]	$a^5D_3 - y^5P_2^0$	31	50	3.0
271.9[c]	$a^5D_4 - y^5P_3^0$			
252.7[c]	$a^5D_3 - x^5D_3^0$	35	518	0.015
252.3[c]	$a^5D_4 - x^5D_4^0$			
249.1[c]	$a^5D_2 - x^5F_3^0$			
249.0[c]	$a^5D_0 - x^5F_1^0$			
248.8[c]	$a^5D_3 - x^5F_4^0$			
248.3[c]	$a^5D_4 - x^5F_5^0$	100	1000	0.009

[a] Lowest state is a^5D_4.
[b] Relative to 248.3 nm.
[c] Unresolved lines.
[d] Uncorrected for response characteristics of photomultiplier.

the resonance lines of the iron atom spectrum. The relative intensities of the most useful iron resonance lines obtained with the above operating conditions are shown in Table I.

Reagents

Iron stock solution. A 1000-p.p.m. stock solution of iron was prepared by dissolving 7.136 g of iron(II) ammonium sulphate (A.R. grade) in 1 l of 0.5 *M* sulphuric acid. This solution was diluted as required before use.

Diverse ions. Solutions of diverse ions were prepared from analytical-reagent-grade salts.

Optimum operating conditions

When 10 and 100-p.p.m. iron solutions were nebulised into the air–acetylene flame with the electrodeless discharge tube source in operation, atomic fluorescence signals were observed at each of the wavelengths shown in Table I. The most intense fluorescence was obtained at the 248.3-nm and 372.0-nm lines. Owing to the low flame background and the very small iron thermal emission at 248.3 nm, this wavelength was selected for all further analytical work.

The effect of variation of acetylene flow-rate between 1.0 and 1.5 l/min on the fluorescence intensity at 248.3 nm was studied. The burner height was adjusted so that the monochromator entrance slit viewed the interconal zone of the flame between 4 and 24 nm above the primary zone. The most intense fluorescence was obtained with an acetylene flow-rate of 1.1 l/min, while the air flow-rate was maintained constant at

7.0 l/min, the fluorescence decreasing considerably at acetylene flow-rates of 1.0 and 1.2 l/min.

With the optimum acetylene flow-rate, the effect of variation of the height of observation in the flame on the atomic fluorescence intensity at 248.3 nm was investigated. A steady decrease in analytical signal was observed as the height of the burner was lowered in relation to the monochromator entrance slit, and the burner was therefore positioned so that the slit viewed the emitted radiation immediately above the primary reaction zone without receiving radiation from this zone itself. The monochromator slit-width was varied under otherwise optimum operating conditions.The slit-width which gave the most favourable signal-to-background and noise ratio at 248.3 nm was found to be 0.2 mm (corresponding to a spectral band-width of *ca.* 0.8 nm).

Calibration data and detection limits

With the optimum operating conditions, linear atomic fluorescence calibration graphs were obtained at 248.3 nm over the range 0.1–40 p.p.m. The 248.3-nm iron line is also the strongest absorption line, however, and at concentrations greater than 40 p.p.m., the calibration graphs exhibit curvature towards the concentration axis owing to self-absorption. Linear atomic fluorescence calibration graphs may be obtained for higher concentrations of iron when the less strongly absorbing 372.0-nm line is employed. The detection limits obtained at each of the nine lines for which atomic fluorescence was observed are shown in Table I. The detection limits are defined as that concentration of iron in aqueous solution which produces a signal-to-noise ratio of unity.

Interference studies

The interference effects on the atomic fluorescence intensity from a 10-p.p.m. iron solution at 248.3 nm produced by various cations and anions were examined. No interference was caused by 1000-fold amounts of Co, Hg, Ta, or by 100-fold amounts of Co, Cr(VI), Mo, Cd, Al, Zn, Hg, Pb, Ta or Ti. Negative errors of less than 5% were caused by 1000-fold amounts of Ni, Mo, Cu, Al or Pb. Positive errors of less than 5% were caused by 100-fold amounts of Th or 200-fold amounts of W. Negative errors of less than 10% were caused by 1000-fold amounts of Th, Cd, or PO_4^{3-}, or by 100-fold amounts of Cu, V or Mn. Zirconium in 100-fold amount caused a positive error of *ca.* 10%. Large negative errors were obtained in presence of 1000-fold amounts of V, Mn and Zn.

It is probable that the slight reductions in signal for iron obtained in the most concentrated solutions (10 mg/ml) may be caused by their reduction of the nebuliser efficiency. Very little positive interference was caused by scattering of the radiation from the source by particulate matter in the flame. Only in the case of the most refractory elements (Th, W and Zr) was appreciable scatter detected at 248.3 nm.

Atomic absorption and flame emission measurements

A brief study of the atomic absorption spectrophotometry of iron was made with the same apparatus as described for fluorescence measurements. For atomic absorption measurements, however, the modulated electrodeless discharge tube source was employed with the SP 900A flame spectrophotometer in the "absorption" mode with the source radiation focussed onto the entrance slit of the monochromator. In this way a convergent beam of radiation was made to pass through an air–acetylene flame using the standard 10-cm path absorption burner fitted to the commercial instrument. When burner height and flame mixture strength were optimised, the calibration graph at 248.3 nm was linear between 1 and 40 p.p.m., and the extrapolated concentration required to produce 1% absorption was 0.9 p.p.m. The limit of detection (signal: noise, peak-to-peak = 1) for an aqueous iron solution was found to be *ca.* 0.1 p.p.m. The calibration graph is similar to that reported by MARSHALL AND WEST[10].

Flame atomic emission measurements were made for iron with the burner assembly employed for fluorescence measurements and no electrodeless discharge tube source. The SP 900A was used in the "emission" mode, *i.e.* with a mechanical chopper interposed between the flame and the monochromator, to modulate the iron atomic emission and produce an a.c. current from the photomultiplier suitable for amplification. This signal is not amplified when fluorescence measurements are made with the source and detector operating at 50 Hz. The obtainable detection limits for iron by emission spectrophotometry under optimum conditions are 3 p.p.m. and 0.4 p.p.m. at 248.3 and 372.0 nm respectively. The detection limit data for the three techniques are summarised in Table II.

TABLE II

DETECTION LIMITS FOR IRON WITH APPARATUS EMPLOYED

Wavelength (nm)	*Detection limits (p.p.m.)*		
	Atomic fluorescence	*Atomic absorption*	*Flame emission*
248.3	0.009	0.1	3
372.0	0.84	1.5	0.4

Conclusion

Iron may be determined with high sensitivity and good selectivity by measurement of the atomic fluorescence at 248.3 nm in an air–acetylene flame excited by intense and stable microwave discharge tube sources. This study indicates that the sensitivity of the determination of iron by a.f.s. is *ca.* one order of magnitude greater than the sensitivity for the atomic absorption method; the two techniques possess similar selectivity.

While this paper was being prepared, an atomic fluorescence study of iron, cobalt and nickel with high-intensity lamps of the Sullivan and Walsh type was reported by MATOUSEK AND SYCHRA[14]. Their results for iron are closely similar to those reported above, but direct comparison is difficult, as the relative intensities of the two sources are not known and the instrumental sensitivities are different. On the basis of the available data and our experience with the same instrumentation, however, it appears that the electrodeless discharge tube source may be considerably more intense at 248.3 nm than the high-intensity hollow-cathode lamp.

Chemistry Department,
Imperial College,
London, S. W. 7 (England)

L. EBDON
G. F. KIRKBRIGHT
T. S. WEST

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Separation of rhenium from molybdenum, tungsten, vanadium and some other elements by extraction with isoamyl alcohol from phosphoric acid–hydrogen peroxide

Rhenium(VII) can be extracted from hydrofluoric acid media with ether[1] and quaternary amines[2], from hydrochloric and sulphuric acids with various oxygenated solvents[3–7] and quaternary amines[2,8], from nitric acid with alcohols[3], butyl phosphates[9] and quaternary amines[2,10] and from perchloric and acetic acids with alcohols[3]. The extraction of rhenium from phosphoric acid media, however, has not received any attention; this acid forms complexes with molybdate, vanadate and tungstate but not with rhenium, hence interesting separations should be possible, particularly since tungstic and silicic acids would be kept in solution without difficulty.

Experimental

Reagents. Rhenium solutions and solutions of other ions were prepared as described previously[11].

Isoamyl alcohol (B.D.H., Ltd) was distilled, the 128–131° portion being used; other solvents were used directly[11].

Samples. Synthetic flue dust was prepared as described previously[11] except that the solution was made up in 1 N phosphoric acid and contained 200 μg of rhenium per 100 ml, the other metal ions being present in mg-amounts. A flue dust from copper manufacture, and molybdenite samples were fused with sodium peroxide–sodium carbonate mixture as described previously[11].

Extraction procedure. Adjust the sample solution, or the filtrate from the fusion treatment to 1 N in phosphoric acid and add 1 ml of 30% hydrogen peroxide for each 100 mg of peroxy-forming ion in 20 ml of solution. Shake vigorously with four portions of isoamyl alcohol, each portion being the same volume as the solution, for 3 min each time. Neutralize the acid in the combined solvent phases with alkali and back-extract the metal ions with two equal-volume portions of water, shaking for 2 min each time. Evaporate the back-extracts to a suitable volume and adjust to pH 4–5 with acetic acid and ammonium acetate. Then extract the small amounts of molybdenum, vanadium, etc., accompanying rhenium as oxinates into chloroform[12]. Rhenium remains quantitatively in the raffinate.

The percentage extraction of individual elements was obtained from their determination in the back-extract after a single extraction with equal volume of solvent from phosphoric acid solutions containing hydrogen peroxide. Absence of extraction was checked by sensitive colour tests.

Determination of the elements. Microgram amounts of rhenium were determined colorimetrically by the thiocyanate method[13], the colored complex being extracted into isoamyl alcohol. Milligram amounts were determined gravimetrically by the tetraphenylarsonium chloride method. Small amounts of molybdenum, vanadium, tungsten and other elements were determined colorimetrically[13]. Colour measurements were made with a Spekker Absorptiometer (Hilger and Watts, London) with suitable Kodak filters and 1-cm cells.

Results and discussion

Extraction of rhenium by isoamyl alcohol at different acidities is shown in Table I. Sodium phosphate (0.5 g) or sulphate (3.5 g) in *N* phosphoric acid decreases the extraction by 6–8%, while chloride, oxalate, fluoride, nitrate and acetate decrease it steeply when present in gram-amounts. Isoamyl alcohol extracts 1% Mo, 2.4% V and 15% W from 1 *N* phosphoric acid media and more from higher acidities. The percentage extractions of ions other than rhenium from 1 *N* phosphoric acid are lowered, if the solutions contains 1 ml of 30% hydrogen peroxide for each 100 mg of the ion, the rhenium extraction being unaffected. Under these conditions, the percentage extractions are: 0.42 V, 0.45 Mo, 0.62 W, 0.48 Se, 4.4 Si and only 0.01 U, 0.015 Os and 0.067 Fe, while Cr, Co, Ni, Cu and Te are not extracted. Thus, four isoamyl alcohol extractions from this medium remove rhenium quantitatively, accompanied by only ca. 2% each of Mo, V, W, Se, and traces of U, Os and Fe. The ions are back-extracted and the residual molybdenum, vanadium, tungsten, uranium and iron are removed as oxinates by extraction into chloroform at pH 4–5. In the raffinate, rhenium is determined by the thiocyanate method. Any selenium, silica and osmium surviving from 100 mg of their original amounts, do not interfere. The estimated loss of rhenium is less than 1%.

TABLE I

PERCENTAGE EXTRACTION OF RHENIUM FROM PHOSPHORIC ACID SOLUTION
(without peroxide addition)

H_3PO_4 (*N*)	0	1	3	4	7	8	9
With isoamyl alcohol	2	78	83	90	91	—	91
With TBP	—	27	—	36	—	—	—
With MIBK	—	42	—	71	—	85	—

Table II shows the wide variety of samples that can be handled by the method with satisfactory results. Flue dusts, molybdenites and rhenium alloys containing molybdenum, vanadium, cobalt, nickel, chromium or copper, can all be analysed; the

TABLE II

ANALYSIS OF SAMPLES BY THE PROPOSED METHOD

Sample composition						*Re found (µg)*
Mo (mg)	*V (mg)*	*W (mg)*	*Se (mg)*	*Os (mg)*	*Re (µg)*	
500	—	—	—	—	25	24.5
—	200	—	—	—	42	41.0
—	—	200	—	—	35	34.5
—	—	—	30	—	20	19.5
—	—	—	—	100	30	29.0
200	40	48	4	7.5	40[a]	39.0
Synthetic flue dust a					24	23.5
Synthetic flue dust b					30	29.5
Molybdenite Cananea (Mexico)					0.012%[b]	0.011%
Molybdenite (Canada)					0.00204%[b]	0.0019

[a] Plus 10 mg Cu, 6 mg Ni and 6 mg Co.
[b] Reported value.

method is of special value when the samples contain tungsten and/or silicon, as they are kept in solution by the phosphoric acid and are little extracted by the solvent.

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Chemistry Department,
Kurukshetra University,
Kurukshetra (India)

V. YATIRAJAM
L. R. KAKKAR

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Spectrophotometric determination of osmium with 2-aminocyclopentene-1-dithiocarboxylic acid

Thiourea and several of its derivatives have long been used for spectrophotometric determination of osmium[1]. Among the various other reagents that have been recommended for osmium[1], there are relatively few other thio-containing compounds, but *o*-(β-benzoylthiourido)benzoic acid[2], a derivative of thiourea has been recently used with success.

The present communication describes the use of 2-aminocyclopentene-1-dithiocarboxylic acid for the spectrophotometric determination of osmium. The reagent forms a reddish brown complex at pH 3.5–4 with osmium, which is soluble in many organic solvents. The reaction is sensitive and the coloured system obeys Beer's law at 470 nm from 0.5 to 16 p.p.m.

Apparatus and reagents

A Hilger Uvispek spectrophotometer was used with 1-cm cells.

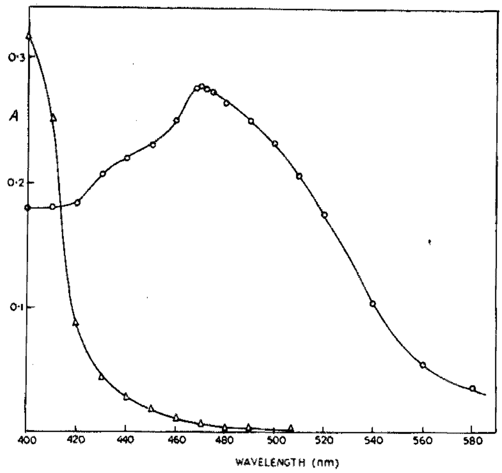
A standard solution of osmium was prepared from its tetroxide as previously described[3].

The reagent was prepared by the method of YOKOYAMA AND TAKESHIMA[4]. A 0.5% solution of the reagent in 95% ethanol was used.

All other reagents used were of high purity.

Procedure

To a measured quantity of osmium solution, add 1 ml of the reagent and add dilute hydrochloric acid so that the pH will be 3.5–4 after dilution to 25 ml with 95% ethanol. After 10 min, measure the absorbance at 470 nm (Fig. 1) against a reagent blank prepared similarly.



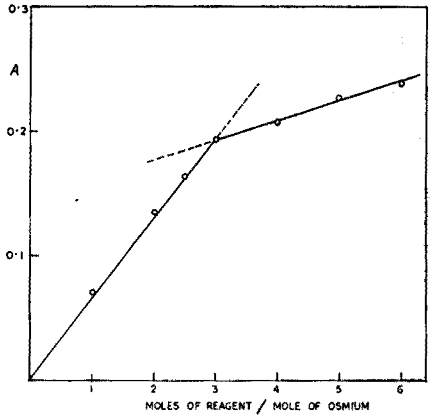


Fig. 1. Absorption spectrum of the osmium complex. (○) Complex, (△) reagent alone.

Fig. 2. Mole ratio method for composition. $5 \cdot 10^{-4}M$ solutions; pH 3.5–4; 470 nm.

Effect of acidity, reagent and time

The optimum pH of the colour system was studied with varying concentrations of dilute hydrochloric acid. The maximum colour intensity was developed only at pH 3.5–4.

For 1–16 p.p.m. of osmium, maximum colour intensity was obtained with 1 ml of the reagent and addition of more reagent had no effect on the system. Colour development was instantaneous at room temperature (30°) and the colour system was found to be stable for 3 h; all absorbances were measured 10 min after addition of the reagent.

Under these conditions, the colour system obeyed Beer's law over the range 0.5–16 p.p.m. of osmium in the final solution.

Composition of the complex

The composition of the complex was determined by JOB's[5] method of continuous variation and by the mole ratio method[6].

For the continuous variation method, equimolar solutions ($1 \cdot 10^{-3}\,M$) of osmium and reagent were used. The maximum indicated that in solution the metal and reagent combine in the ratio of 1:3. This ratio was confirmed by the mole ratio method (Fig. 2).

An estimate of the dissociation constant of the complex was obtained from Job curves in the usual manner, the osmium solutions being $2\text{–}5 \cdot 10^{-4}\,M$ and the reagent solution $10^{-3}\,M$. The mean value found was $4.0\ (\pm 0.9) \cdot 10^{-10}$.

Interference of diverse ions

Interferences of foreign ions are as follows (the amounts in p.p.m. of ion that can be tolerated are given in parentheses):
Rh^{3+} (200), Ru^{3+} (400), Mn^{2+} (400), Cr^{3+} (500), UO_2^{2+} (500), Be^{2+} (400), Sr^{2+} (400), Ba^{2+} (500), Ca^{2+} (500), Mg^{2+} (500), Sn^{2+} (500), Al^{3+} (500), La^{3+} (500), rare earth (500), Pb^{2+} (400), Zn^{2+} (200), Au^{3+} (500), V^{5+} (500), Bi^{3+} (200), As^{5+} (400), Sb^{3+} (400) and Cd^{2+} (400);
even 400 p.p.m. of citrate, oxalate, EDTA, tartrate, and phosphate do not interfere. The main interferences are Fe^{3+}, Cu^{2+}, Ni^{2+}, Pd^{2+} and Pt^{4+}.

Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science,
Jadavpur,
Calcutta-32 (India)

N. K. DUTT
T. SESHADRI

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ANNOUNCEMENT

PRELIMINARY ANNOUNCEMENT OF 1970 PITTSBURGH CONFERENCE

The Twenty-first Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held in Cleveland, Ohio, U.S.A., March 1–6, 1970. The headquarters for the meeting will be the Cleveland Convention Center. An estimated 300 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. Symposia on the following subjects are now being arranged.

1. SSP Award Symposium on Absorption Spectroscopy
2. Coblentz Society Symposium on Laser Raman Spectroscopy
3. Analytical Techniques on the Horizon
4. Polymer Characterization
5. Analytical Chemistry — A Fading Discipline?
6. Computers in the Analytical Laboratory
7. High Speed Chromatography (Gas and Liquid)
8. Analyses of Gases and Vapors
9. Recent Developments in X-ray and Optical Spectroscopy
10. Analytical Techniques in Space
11. Molecular Spectroscopy of Minerals and Related Inorganics

Papers are *not* restricted to the symposium topics and original papers on *all* phases of analytical chemistry and spectroscopy are invited.

Authors who wish to present papers at the 1970 Pittsburgh Conference should submit three copies of a 150 word abstract and include the names and addresses of the authors, and the name of the laboratory in which the work was done. Abstracts should be sent to: EDWARD L. OBERMILLER, Consolidation Coal Company, Research Division, Library, Pa. 15129, U.S.A.

The final date for receipt of abstracts is *October 1, 1969*.

In addition to the program of technical papers, there will be an exhibition of the newest analytical instrumentation. More than 250 companies will display instruments, chemicals and equipment. A complete program of activities for wives and lady attendees at the Conference is also being planned for the 1970 Pittsburgh Conference.

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School of Pharmacy
Pittsburgh, Pa. 15219, U.S.A.

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