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Editors
PHILIP W. WEST *(Baton Rouge, La., U.S.A.)*
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In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1971. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. 53, No. 1	January 1971	
Vol. 53, No. 2	February 1971	**(completing Vol. 53)**
Vol. 54, No. 1	March 1971	
Vol. 54, No. 2	April 1971	
Vol. 54, No. 3	May 1971	**(completing Vol. 54)**
Vol. 55, No. 1	June 1971	
Vol. 55, No. 2	July 1971	**(completing Vol. 55)**
Vol. 56, No. 1	August 1971	
Vol. 56, No. 2	September 1971	
Vol. 56, No. 3	October 1971	**(completing Vol. 56)**
Vol. 57, No. 1	November 1971	
Vol. 57, No. 2	December 1971	**(completing Vol. 57)**

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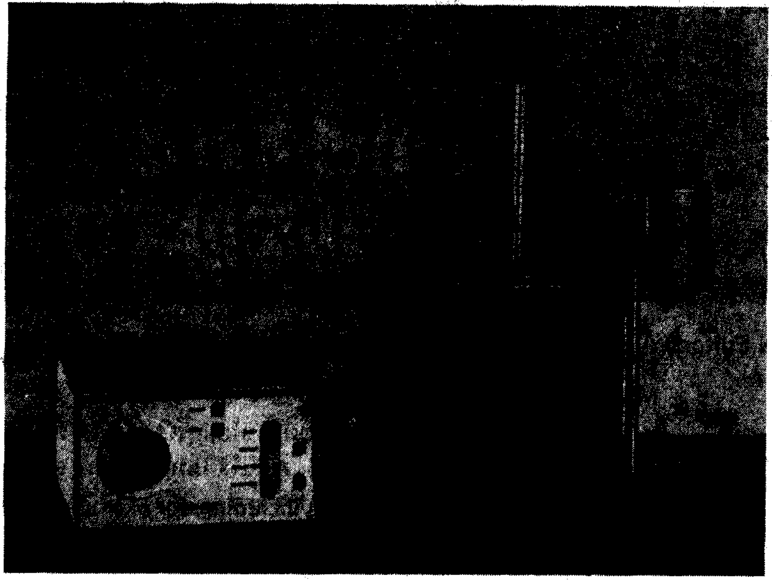

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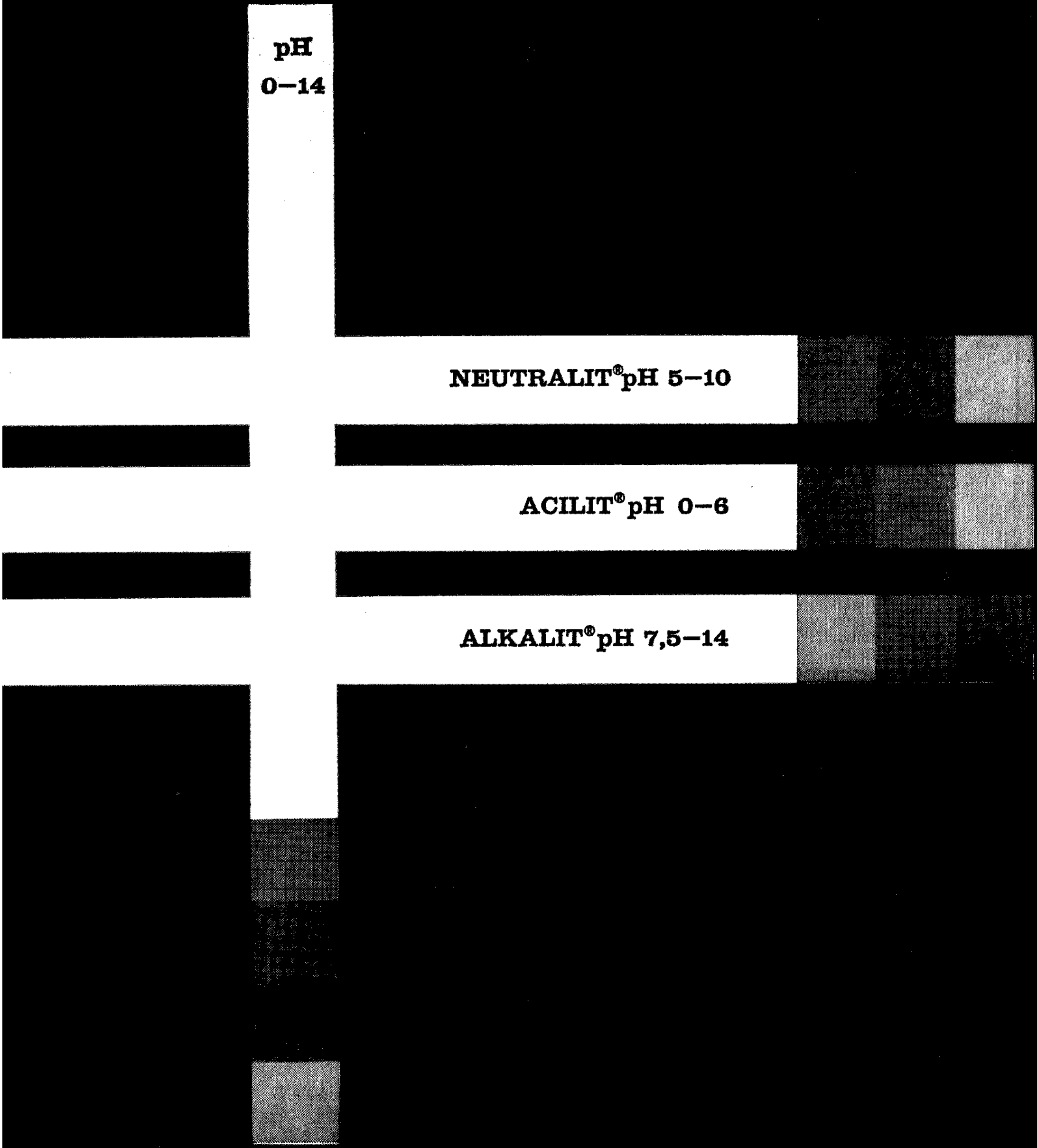
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 52, No. 1, October 1970

A SPECTROPHOTOMETRIC REACTION-RATE METHOD FOR DETERMINATION OF SILICATE AS β-12-MOLYBDOSILICIC ACID

A new method for the determination of silicate is described based on measurement of the initial rate of formation of the heteropoly complex, β-12-molybdosilicic acid, from the reaction of silicate with molybdate–perchloric acid reagent. The relative precision for 3 p.p.m. of silicon was better than 1%, and for 0.3 p.p.m., the lower concentration limit, better than 4%. The β-12-molybdosilicic acid is formed under conditions where the reaction rate is independent of the hydrogen-ion concentration. The method is simple and rapid, requiring only 10–30 sec of reaction time. A study of diverse ions is presented.

L. G. Hargis,
Anal. Chim. Acta, 52 (1970) 1–7

SPECTROPHOTOMETRIC DETERMINATION OF TRACE VANADIUM OXYTRICHLORIDE IN TITANIUM TETRACHLORIDE

A simple method is described for determining vanadium(V) as vanadium oxytrichloride in titanium tetrachloride after dissolution in hydrochloric acid. In this system diphenylbenzidine is oxidized by vanadium(V) to produce a violet colored solution. Spectrophotometric measurements are made at 575 nm. The procedure is designed for the measurement of vanadium in titanium tetrachloride at the 2–10 p.p.m. level.

N. C. Radcliffe and J. R. Parker,
Anal. Chim. Acta, 52 (1970) 9–14

A CRITICAL STUDY OF THE MOLAR ABSORPTIVITY OF IRON(III) IN SULPHURIC ACID MEDIUM

EFFECT OF TEMPERATURE

(in French)

The molar absorptivity of iron(III) at 303 nm and 25° in 0.4 M sulphuric acid has been studied. The value was found to be 2239 ± 2 $l\ mol^{-1}\ cm^{-1}$, and the effect of temperature on the absorptivity was 0.66% per degree between 20 and 30°. These values may vary according to the instrumentation used. Standard solutions must be prepared and standardized with great care and the spectrophotometer cells must be properly thermostated, otherwise errors of several per cent may occur.

F. Dejehet, F. Coget, J. Cara, D. Apers and P. Capron,
Anal. Chim. Acta, 52 (1970) 15–23

THE COULOMETRIC TITRATION OF BARBITURATES

Constant-current coulometry has been applied to the titration of barbituric acid derivatives, *i.e.*, sodium phenobarbital, sodium seconal, sodium barbital, and sodium sandoptal. The titrant is generated mercury(II). The titration may be performed in aqueous potassium nitrate–acetone, or aqueous sodium perchlorate–acetone solutions. The most sensitive systems are the partially nonaqueous ones, with both supporting electrolytes giving similar results. Comparable results also were obtained at room temperature and at 37°. Considerable evidence has been obtained to support the theory that mercury(II) is not generated directly in these media, but is formed from the disproportionation of mercury(I) into the element and mercury(II). Qualitative tests proved the presence of all three species in the titration medium. Structural analysis of the compound formed in the coulometry cell was performed, and with sodium phenobarbital the evidence indicates that a polymeric compound containing continuous Hg–N linkages is formed. The evidence for the other compounds is less conclusive, probably because a mixture of products is formed in the titration cell.

J. R. Monforte and W. C. Purdy,
Anal. Chim. Acta, 52 (1970) 25–33

COMPLEXIMETRIC TITRATION OF GALLIUM WITH COPPER–EDTA–TAR AS INDICATOR

A copper–EDTA–TAR system is proposed for the compleximetric titration of gallium. The recommended procedure for the titration was established from theoretical considerations on the equilibria involved. The color change is from lilac to light green in an acetate-buffered solution at pH 3.5–4. The method is simple and accurate for the titration of solutions containing 1–20 mg Ga per 100 ml.

H. Yamada, I. Kojima and M. Tanaka,
Anal. Chim. Acta, 52 (1970) 35–40

POTENTIOMETRIC STUDIES WITH A LIQUID ION-EXCHANGE LEAD-SELECTIVE ELECTRODE

The performance of the Orion liquid ion-exchange lead-selective electrode has been determined in terms of the working concentration range of lead ions, its selectivity to other ions, its response time, the effective pH range in which it can be used, and its use in potentiometric titrations. The electrode exhibits relatively high response to monovalent cations and can be used in the potentiometric titration of alkali metal, thallium(I), silver(I), and ammonium ions with sodium tetraphenylboron, as well as for titrations of lead(II) with various solutions.

S. Lal and G. D. Christian,
Anal. Chim. Acta, 52 (1970) 41–46

OXIDATION AND COMBUSTION REVIEWS

edited by **C. F. H. TIPPER,** *Senior Lecturer in the Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, England*

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APPLICATION OF SILICONE RUBBER-BASED GRAPHITE ELECTRODES FOR CONTINUOUS FLOW MEASUREMENTS

PART II. VOLTAMMETRIC STUDY OF ACTIVE SUBSTANCES INJECTED INTO ELECTROLYTE STREAMS

A technique has been developed for the rapid analysis of samples injected into a streaming supporting electrolyte in small volumes. At constant potential the peak area of the voltammetric signal is proportional to the amount of electroactive material injected. The parameters of the determination were studied and interpreted theoretically. The experimental results are in good agreement with theory.

G. Nagy, Zs. Fehér and E. Pungor,
Anal. Chim. Acta, 52 (1970) 47–54

ACID–BASE REACTIONS IN TRIFLUOROACETIC ACID AND OTHER ACID MEDIA

COMPARISON OF THE RELATIVE STRENGTH OF ACIDS AND BASES

(in French)

The classification of the relative strengths of 25 uncharged bases in trifluoroacetic acid is compared with those established in acetic acid and water–sulphuric acid mixtures. The pK_{H_2O} values of the following acids, which are strong in water, have been determined: perchloric acid, −7.7; sulphuric acid, −6.0; chlorosulphuric acid, −5.9; methanesulphuric acid, −5.4; *p*-toluenesulphonic acid, −5.4; hydrobromic acid, −5.2; fluoroboric acid, −4.9; hydroiodic acid, −4.5; hydrochloric acid, −3.7; nitric acid, −4.3.

J. Bessière,
Anal. Chim. Acta, 52 (1970) 55–63

DETERMINATION OF SOLUBLE CARBOHYDRATES IN SEA WATER BY PARTITION CHROMATOGRAPHY AFTER DESALTING BY ION-EXCHANGE MEMBRANE ELECTRODIALYSIS

A method for the determination of different soluble sugars in sea water is discussed. An apparatus for desalting the sea water by electrodialysis with ion-exchange membranes is described. The desalted samples are evaporated *in vacuo* and investigated by liquid–liquid and gas–liquid chromatographic methods. These methods are compared and the former is shown to be superior for the determination of different sugars. With the liquid–liquid partition chromatographic method, eight monosaccharides were determined in the range of 0.15–46.5 $\mu g\ l^{-1}$; small amounts of sorbose, fucose, sucrose, ethylene glycol and glycerol were also detected.

B. O. Josefsson,
Anal. Chim. Acta, 52 (1970) 65–73

ENZYMATIC METHODS OF ANALYSIS

TRACE ANALYSIS OF VARIOUS PESTICIDES WITH INSECT CHOLINESTERASES

The effect of fifteen different pesticides including carbamates, chlorinated hydrocarbons and organophosphorus compounds on cholinesterase from housefly, sugar boll weevil, fire ant and German cockroaches is reported. Since the cholinesterase from each source shows different inhibition by various inhibitors, an increase in the specificity of enzyme systems for the determination of pesticides is possible.

G. G. Guilbault, M. H. Sadar, S. S. Kuan and D. Casey,
Anal. Chim. Acta, 52 (1970) 75–82

THERMAL DEHYDRATION OF SOME 8-QUINOLINOL CHELATE HYDRATES

The thermal dehydration of the 8-quinolinol chelate hydrates of Ni(II), Co(II), Cu(II), Cd(II), Mn(II), Mg(II), and Zn(II) was studied by thermogravimetry, differential scanning calorimetry, h.t.r.s. and d.r.s. Calorimetric data indicated that the heats of dehydration were correlatable with crystal field and electrostatic theory. The thermogravimetric data, applied in a different type of solid state kinetics equation, indicated that there was a difference in type of water bonding between that in the magnesium(II) complex and the other complexes. Changes in reflectance spectra upon dehydration were ascribed to possible changes in coordination for the complexes of Co(II), Cu(II), and Ni(II), involving the *d*-orbital splittings, and to changes in coordination affecting charge transfer in the complexes of Mg(II), Zn(II), and Cd(II).

R. H. Gore and W. W. Wendlandt,
Anal. Chim. Acta, 52 (1970) 83–89

THE DETERMINATION OF TIN IN GEOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Tin can be determined in geological samples by atomic absorption spectroscopy by using a 45-cm long-heated absorption tube. After decomposition by fusion and electrodeposition separation, the method is sufficiently accurate and precise down to 2 p.p.m. of tin in silicate or sulphide samples. The behaviour of tin in the absorption tube, and cationic and anionic interferences were studied.

B. Moldan, I. Rubeška, M. Mikšovský and M. Huka,
Anal. Chim. Acta, 52 (1970) 91–99

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

The mean amplitudes have proved to play an increasingly important role as structural parameters (in addition to the rigid-molecule parameters) in modern studies of molecular structure. These parameters have been applied most extensively in gas electron diffraction, and also calculated by spectroscopic methods from infrared and Raman data.

The book reviews completely the previous work on mean amplitudes of vibration, including 476 references. Furthermore the spectroscopic analysis of harmonic vibrations of polyatomic molecules is reconsidered. The survey includes known methods based on the Wilson G and F matrices, but also supplementary aspects and new material, particularly as regard to the compliants ('inverse' force constants), Coriolis coupling and Σ matrices.

Seventeen molecular models are treated in great detail, giving G and C^{a} matrix elements and other useful expressions for subsequent applications and future reference.

Throughout the book special emphasis is laid on the calculation and properties of mean amplitudes of vibration and related quantities such as the generalized mean-square amplitudes and shrinkage effects. An additional 380 references are cited.

As a whole the book is to be regarded as a standard reference for spectroscopic analysis of polyatomic molecules based on the approximation of small harmonic vibrations with its application to mean amplitudes as one of the particular features. The last chapter contains eome proposals on future work in the field, including higher order approximations.

The book is believed to be of interest for advanced students and research workers on molecular structure (especially by gas electron diffraction), and spectroscopists interested in theoretical aspects and applications of spectral data.

CONTENTS: 1. Introduction - 2. Review of previous work - 3. Molecular vibrations: survey and notation - 4. Theory of compliance matrices - 5. Quantum–mechanical considerations - 6. Coriolis coupling of vibration–rotation: a survey - 7. Theory of the mean–square amplitude matrix - 8. Preliminary treatment of simple molecular models - 9. Mean–square amplitude matrices of simple molecular models - 10. Numerical examples of mean–square amplitude quantities and their variations - 11. Arbitrary interatomic distances and mean amplitudes of vibration - 12. Mean amplitudes of vibration of individual molecules - 13. Perpendicular displacements and generalized mean–square amplitudes - 14. Theory of the Bastiansen–Morino shrinkage effect - 15. Bastiansen–Morino shrinkage effects of individual molecules - 16. Coriolis constants and mean–square amplitude quantities - 17. Conclusion and future prospects - Bibliography - References and author index - Subject index

7x10", viii + 430 pages, 157 tables, 45 illus., 1968, Dfl. 75,00, £10

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A FLAME EMISSION TECHNIQUE FOR OBTAINING STRUCTURAL INFORMATION FROM ORGANIC MOLECULES

The use of an entrained air–hydrogen flame to obtain structural information of amines and alcohols was studied. Differences in emission intensities of CH, C_2, and CN species indicate the possibility of qualitative analysis of organic compounds. A linear relationship was found to exist for members of different homologous series of amines and alcohols, when the intensity of CH emission was plotted *vs.* intensity of C_2 or CN emission.

J. J. Kroeten, H. W. Moody and M. L. Parsons,
Anal. Chim. Acta, 52 (1970) 101–108

STUDIES OF THE CARBON CONTENT OF STEEL AND ITS DEPTH DISTRIBUTION BY MEANS OF PROTON ACTIVATION ANALYSIS

The carbon content and depth distribution close to the surface in steel samples at the 0.1–1% level have been studied, by means of proton activation in the energy range 1–4.5 MeV. A Van de Graaff accelerator was used, initiating the nuclear reaction $^{12}C(p,\gamma)^{13}N$ which possesses two resonances at the energies of 0.46 and 1.70 MeV. The technique is of interest in connection with carbonization of iron products.

D. Brune and R. Hellborg,
Anal. Chim. Acta, 52 (1970) 109–114

REGULARITIES IN THE DISTRIBUTION OF TTA AND ITS SCANDIUM CHELATE INTO A SERIES OF ETHER SOLVENTS

The distribution of a powerful chelating agent, TTA, and its typical trivalent metal chelate, that of scandium(III), between aqueous perchlorate solution ($\mu = 0.1$) and 12 ether solvents was determined at 25°. A good correlation was found between the distribution coefficient of TTA and the "solubility parameter" of the ether solvents, except bis(2-chloroethyl)ether. The distribution coefficient of the scandium chelate (P_M) was compared with that of TTA (P_{HA}), and it was confirmed that the relationship expressed by $\log P_M = n \log P_{HA} + \text{const.}$, is valid for the present system.

N. Suzuki, K. Akiba and H. Asano,
Anal. Chim. Acta, 52 (1970) 115–122

A RAPID POLAROGRAPHIC DETERMINATION OF SULPHIDE

A rapid polarographic method based on the stoichiometric reaction between methylmercury(II) iodide (MeHgI) and soluble sulphide is described for determination of the sulphide ion in aqueous solution; less than 1 p.p.m. of sulphide ion can be determined with a precision of ±5% or better, at pH values greater than 8. Various common anions, with the exception of cyanide ions, do not interfere.

L. C. Gruen,
Anal. Chim. Acta, 52 (1970) 123–127

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POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XVI. POLAROGRAPHIC AND SPECTRAL INVESTIGATION OF ACID–BASE EQUILIBRIA IN AQUEOUS SOLUTIONS OF 2-THIOBARBITURIC ACIDS WITH SUBSTITUENTS ON SULPHUR

2-Methylthiobarbituric acid (I) and 1-ethyl-2-allylthio-5-(2-methylbutyl)barbituric acid (II) have protonation constants of 4.8 and 6.1, respectively; protonation of unsubstituted 2-thiobarbituric acid (III) ($\mathrm{p}K_\mathrm{C} = 2.25$) and its 5-alkyl derivative (IV) ($\mathrm{p}K_\mathrm{C} \simeq 1.0$) occurs at lower pH values. I is reducible in a 2-electron process, followed by a further 6-electron step; the rate constant of the antecedent protonation is of the order of 10^8 l mol^{-1} sec^{-1}. Compounds II, III and IV do not show cathodic waves; the reasons are discussed. Anodic waves corresponding to formation of mercury compounds are formed by the unprotonated species. Reduction waves of compound I, and u.v. absorption bands and anodic waves of compounds I–IV are suitable for analytical purposes.

W. F. Smyth, G. Svehla and P. Zuman,
Anal. Chim. Acta, 52 (1970) 129–138

CORRELATIONS BETWEEN ^{31}P N.M.R. CHEMICAL SHIFTS AND STRUCTURES OF SOME ORGANOPHOSPHORUS PESTICIDES

(Short Communication)

R. T. Ross and F. J. Biros,
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DETERMINATION OF LOW CONCENTRATIONS OF ORGANIC CARBON IN PHOSPHORIC ACID AND PHOSPHATE ROCK

(Short Communication)

J. Wimberley,
Anal. Chim. Acta, 52 (1970) 142–145

A NEW SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH 4-(2-THIAZOLYLAZO)-RESORCINOL

(Short Communication)

T. Shimizu and E. Momo,
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by A. B. P. LEVER, Associate Professor of Chemistry,
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A SPECTROPHOTOMETRIC REACTION-RATE METHOD FOR DETERMINATION OF SILICATE AS β-12-MOLYBDOSILICIC ACID

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(Received May 9th, 1970)

Spectrophotometric methods for the determination of silicate based on the formation of yellow 12-molybdosilicic acid[1,2] or a reduced heteropoly blue[3–5] are common and well established in the literature. In addition, a variety of modifications of these basic methods have been developed[6,7]. Unfortunately, the earlier literature failed to recognize the existence of two isomers of 12-molybdosilicic acid and the importance of certain solution conditions in dictating which isomer is formed. STRICKLAND[8] was the first to demonstrate clearly that the acid/molybdate ratio is critical: β-12-molybdosilicic acid is formed in solutions acidified with at least 2 moles of acid per mole of molybdate while α-12-molybdosilicic acid is formed in solutions acidified with less than 1.5 moles of acid per mole of molybdate.

Most analytical methods are based on the formation of the β-isomer[8] in order to take advantage of the greater solution acidity which in turn decreases the number of potential interferences. The β-isomer, however, is not stable and, when formed, spontaneously converts to the thermodynamically favored α-form[8]. This conversion can be slowed but not stopped. STRICKLAND[8] has indicated that it is not possible to obtain a solution of the β-isomer without some α-isomer also present. Since the two isomers have substantially different molar absorptivities at the usual wavelengths of measurement, some error is always introduced. In addition, careful control of the measurement time is also necessary to avoid further error caused by the continuing conversion of the β-isomer. The alternative of waiting at least several hours for complete conversion to the stable α-isomer is distasteful.

The initial reaction-rate method described herein, while perhaps not quite as sensitive as other heteropoly methods, offers the significant advantage of reducing to a negligible extent the error caused by the instability of the β-isomer. In addition it contains the usual advantages offered by reaction-rate methods[9,10].

Rate equation

A kinetic study of the formation of β-12-molybosilicic acid has shown that the formation of the compound can be represented[11] by the reactions:

$$\mathrm{Si(OH)_4 + HMo_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SiO_4\text{–}Mo_2^{4-} + 5H^+}$$

$$\mathrm{SiO_4\text{–}Mo_2^{4-} + 5\,HMo_2^+ \xrightarrow[\text{Slow}]{k_2} \beta\text{-12-isomer} + 5H^+}$$

where HMo_2^+ represents an assumed molybdate dimer[11–13] and SiO_4–Mo_2^{4-} the first intermediate complex formed. The kinetic results did not distinguish steps of the second reaction but a discussion of this fact is unnecessary here. The β-12-molybdosilicic acid absorbs strongly in the visible and ultraviolet spectral regions and absorbance measurements at both 350 and 400 nm conform to Beer's law[1,2]. The rate equation for the formation of β-12-molybdosilicic acid has been determined previously[11] and is given by

$$\frac{\mathrm{d}\,[\beta\text{-isomer}]}{\mathrm{d}t} = \frac{k_1k_2\,[\mathrm{Si(OH)_4}][\mathrm{HMo_2^+}]^6}{k_{-1}[\mathrm{H^+}]^7 + k_2[\mathrm{HMo_2^+}]^5} \tag{1}$$

At low acid concentration, $k_{-1}[H^+]^7 \ll k_2[HMo_2^+]^5$ and eqn. (1) reduces to one of its limiting forms,

$$\frac{\mathrm{d}\,[\beta\text{-isomer}]}{\mathrm{d}t} = k_1[\mathrm{Si(OH)_4}][\mathrm{HMo_2^+}] \tag{2}$$

This condition of low acidity is especially desirable because it produces a reaction rate which is independent of acidity, thereby eliminating the necessity of carefully controlling this often critical parameter. When the initial concentration of molybdate is the same for a series of samples, the initial rate of change of absorbance is directly proportional to the silicate concentration,

$$\left(\frac{\mathrm{d}A}{\mathrm{d}t}\right)_i = K\,[\mathrm{Si(OH)_4}]$$

Optimum solution parameters

The best solution acidity at which to carry out the reaction depends on the amount of molybdate used. In a previous kinetic study[11] where the molybdate concentration was $1 \cdot 10^{-2}$ *M*, the reaction rate was independent of acidity over the range of 0.03–0.07 *M*. At higher acidity the conditions assumed to obtain eqn. (2) are not valid. At acidities around 0.02 *M* a marked change in reaction rate was observed. Presumably this was due to the simultaneous formation of the α-isomer with β-isomer which sets in at the 2:1 acid:molybdate ratio.

The amount of molybdate should be substantially greater than the amount of silicate so as to provide an adequate reaction-rate curve from which to measure the initial reaction rate. Large amounts of molybdate may be required if one wishes to perform the analysis at a high acidity in order to avoid an interference from a particular diverse ion.

Induction period

An induction period preceded the linear reaction-rate period. This period was quite small (3–4 sec) in the absence of diverse ions and probably was mainly the result of mixing phenomena. In the presence of certain diverse ions, particularly the transition metal ions, the induction period was increased to as much as 10–15 sec. Since continuous absorbance *vs.* time curves were recorded, it was easy to determine when the induction period had passed.

Temperature variations had a significant effect on the reaction rate, and therefore all solutions and the spectrophotometer cell compartment were thermostated at 26.00 ± 0.05°.

EXPERIMENTAL

Kinetic measurements

Spectrophotometric kinetic measurements were made on either a Cary 15 or Beckman DB recording spectrophotometer at 350 nm. The reagent blanks exhibited some absorption at this wavelength but this posed no problem since only the rate of change of absorption is desired.

Reagents

All solutions were prepared from reagent-grade chemicals using freshly distilled water and stored in polyethylene bottles to avoid silicon contamination.

The stock molybdate–perchloric acid reagent was prepared from sodium molybdate dihydrate and concentrated perchloric acid to give concentrations of 0.20 *M* molybdate and 0.80 *M* acid. This reagent was allowed to stand at least one day before use.

Sodium silicate stock solutions were prepared by evaporating $Na_2SiO_3 \cdot 9H_2O$ with excess of sodium hydroxide in a platinum crucible, dissolving in freshly distilled water and diluting. The stock solution was standardized by a conventional gravimetric procedure[14]. Monomeric silicon units are most stable in solutions of pH 1–3 and above 13[15]. Diluted stock solutions were adjusted to pH 3 with perchloric acid.

General procedure

Transfer the dissolved sample containing only monomeric silicon units to a small beaker and adjust with dilute sodium hydroxide or perchloric acid to a pH of 3. Exact pH adjustment is unnecessary since a large amount of acid is added later. Transfer the pH-adjusted sample to a suitable volumetric flask, if necessary add sodium perchlorate to obtain a constant ionic strength, and dilute to volume. Transfer exactly 2 ml of the sample to a dry 1-cm cell. Rapidly add 100 μl of the molybdate–acid reagent from a microliter syringe, mix, and place the cell in the spectrophotometer. Record the absorbance at 350 nm *vs.* time until the rate is no longer linear with time (usually 30–60 sec). Distilled water may be used as the reference.

Calculations

A calibration curve is prepared by plotting initial reaction rate *vs.* silicon concentration for a series of known samples. The concentration of unknowns can be read directly from this calibration graph. Initial reaction rates were obtained graphically from the initial slopes of the absorbance *vs.* time curves. In general less than 5% of the total reaction curve was used in evaluating the initial slope. The conditions described in the above procedure are suitable for final concentrations of 0.3–10 p.p.m. of silicon.

RESULTS AND DISCUSSION

Solution variables

The reaction rate is independent of the acidity in the 0.03–0.07 *M* perchloric acid concentration range[11]. Experiments performed by adding the perchloric acid separately with a graduated cylinder were within the limits of precision shown below.

The molybdate concentration must be maintained constant but its value is not particularly important. Excellent results were obtained with molybdate concentrations that were half and twice as large as that suggested in the experimental section. Of course, the reaction rate varies with the molybdate concentration. Some absorbance caused by molybdate is present at 350 nm, but since this absorbance is constant it poses no problem. Larger amounts of molybdate can be used in conjunction with a measurement wavelength of 400 nm where the molybdate absorbance is much smaller.

Standard calibration graph

The standard calibration graph was prepared from standardized silicate solutions of known concentration. The various polymeric forms of silicate react at different rates with molybdate and great care must be taken to insure that the solutions to be measured contain only monomeric silicon units.

A typical calibration curve used in this study was linear from 0.3 to 10 p.p.m. silicon, having a slope of $(7.14 \pm 0.13) \cdot 10^3$ A l mole^{-1} min^{-1} and an intercept of -0.020 A min^{-1} where A represents absorbance. Typical reaction rates varied from 0.050 to 2.20 A min^{-1}.

Effect of ionic strength

Increasing ionic strength had a slight decreasing effect on the reaction rate. Samples containing ionic concentrations as great as about 20% of the acidity used should be treated with a constant large excess of an inert electrolyte such as sodium perchlorate. Similar treatment must be accorded to standard samples.

Precision and accuracy

An indication of the accuracy obtainable is shown in Table I. The calibration plot used was prepared from fourteen solutions of known concentration. These data show that an accuracy of better than 2% can be expected from simple aqueous systems. An estimate of the precision of the analysis was obtained from the results of replicate samples. Eleven replicate analyses of a solution containing 3.36 p.p.m. of silicon showed an average reaction rate of 0.824 ΔA min^{-1} with a standard deviation of $8.0 \cdot 10^{-3}$ (relative standard deviation 0.97%). The practical lower limit was about 0.3 p.p.m. silicon and samples at this concentration could be measured with *ca.* 4% relative error. The rate measurements described here, made by manually determining

TABLE I

ACCURACY OF RESULTS

Measured reaction rate (ΔA min^{-1})	*Silicon concentration*		
	Taken (p.p.m.)	*Found (p.p.m.)*	*% Error*
0.140	0.560	0.548	− 2.1
0.362	1.40	1.42	+ 1.4
0.571	2.24	2.23	− 0.5
1.073	4.20	4.20	0
2.152	8.40	8.43	+ 0.4

the initial slopes of recorded absorbance *vs.* time curves, are ordinarily subject to some operator bias. The method should be quite applicable to automated procedures which are somewhat less time-consuming and less subject to operator bias[16,17].

Diverse ions

The effect of numerous diverse ions was studied for the basic procedure described in the experimental section for the analysis of 3.36 p.p.m. silicon. All solutions, including the control solutions, were made 0.2 *M* in sodium perchlorate to minimize changes in ionic strength on the addition of the diverse ions. An error of less than 2.5% was considered negligible. The results of this study are summarized in Table II.

TABLE II

EFFECT OF DIVERSE IONS

Ion	*Added as*	*Tolerance (p.p.m.)*	*Ion*	*Added as*	*Tolerance (p.p.m.)*
Na^+	$NaNO_3$	$>4,000$	F^-	NaF	50
K^+	KNO_3	3,000	Cl^-	$NaCl$	3,000
NH_4^+	NH_4NO_3	3,000	Br^-	$NaBr$	2,400
Mg^{2+}	$Mg(NO_3)_2$	$>4,000$	ClO_4^-	$NaClO_4$	$>4,000$
Ca^{2+}	$Ca(NO_3)_2$	$>4,000$	NO_3^-	$NaNO_3$	$>4,000$
Al^{3+}	$Al(NO_3)_3$	$>4,000$	$C_2H_3O_2^-$	$NaC_2H_3O_2$	$>4,000$
Fe^{3+}	$Fe(NO_3)_3$	50	SO_4^{2-}	Na_2SO_4	2,000
Ni^{2+}	$Ni(NO_3)_2$	$>4,000$	AsO_4^{3-}	Na_2HAsO_4	25
Cu^{2+}	$Cu(NO_3)_2$	$>4,000$	PO_4^{3-}	NaH_2PO_4	10
Zn^{2+}	$Zn(NO_3)_2$	$>4,000$			

Iron(III) interferes seriously because of its strong absorbance at 350 nm. The strong interference of fluoride is undoubtedly due to its ability to form a complex with the molybdenum(VI). The phosphate and arsenate interferences are expected since both form heteropoly complexes similar to 12-molybdosilicic acid. One interesting feature was noted with the phosphate and arsenate interferences; at high concentrations of phosphate and arsenate (*ca.* 1,000 p.p.m.) the absorbance was decreased to a value close to that of the molybdate blanks and was constant with time. At lower concentration (*ca.* 100 p.p.m.), the absorbance was constant with time but very large. Such events suggest that definite complexes may be formed at low molybdate-to-phosphate or arsenate ratios which have very different absorption characteristics from the ordinary 12-polyacids.

Advantages of the rate method

This reaction-rate method has many advantages over conventional spectrophotometric methods based on similar chemical systems. In the rate method it is not necessary to make absorbance measurements at a very carefully selected time in order to compensate empirically for the effects of the spontaneous β- to α-isomer conversion. Corrections for reagent blank absorbance are unnecessary and the presence of diverse substances that absorb at the measurement wavelength or that impart a turbidity to the solution will not normally interfere. These advantages coupled with the excellent precision and good sensitivity obtainable should make this a very useful method.

SUMMARY

A new method for the determination of silicate is described based on measurement of the initial rate of formation of the heteropoly complex, β-12-molybdosilicic acid, from the reaction of silicate with molybdate–perchloric acid reagent. The relative precision for 3 p.p.m. of silicon was better than 1%, and for 0.3 p.p.m., the lower concentration limit, better than 4%. The β-12-molybdosilicic acid is formed under conditions where the reaction rate is independent of the hydrogen-ion concentration. The method is simple and rapid, requiring only 10–30 sec of reaction time. A study of diverse ions is presented.

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage des silicates; elle est basée sur la mesure de la vitesse de formation initiale de l'hétéropolycomplexe, acide β-12-molybdosilicique, à partir du silicate et du réactif, molybdate–acide perchlorique. La précision relative est supérieure à 1% pour 3 p.p.m. de silicium et 4% pour 0.3 p.p.m. On travaille dans des conditions où la vitesse de réaction est indépendante de la concentration en ions hydrogène. La méthode est simple et rapide et ne demande que 10 à 30 sec.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Bestimmung von Silicat beschrieben. Sie beruht auf der Messung der anfänglichen Reaktionsgeschwindigkeit, mit der sich der Heteropolykomplex β-12-Molybdatokieselsäure aus Silicat und Molybdat–Perchlorsäure-Reagenz bildet. Die relative Genauigkeit für 3 p.p.m. Silicium war besser als 1% und für 0.3 p.p.m., die untere Konzentrationsgrenze, besser als 4%. Die β-12-Molybdatokieselsäure wird unter Bedingungen gebildet, bei denen die Reaktionsgeschwindigkeit von der Wasserstoffionenkonzentration unabhängig ist. Die Methode ist einfach und schnell und erfordert nur 10–30 Sek der Reaktionszeit. Der Einfluss verschiedener Ionen wurde untersucht.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACE VANADIUM OXYTRICHLORIDE IN TITANIUM TETRACHLORIDE

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A method of determining trace vanadium oxytrichloride in anhydrous titanium tetrachloride was required, which would be simple, rapid, and sensitive to vanadium(V) at the 1-p.p.m. level. Several simple methods were considered and evaluated.

A strong fundamental stretching band for V=O has been reported to occur at 9.66 μm[1]. Titanium tetrachloride also absorbs in this region, hence the determination of vanadium oxytrichloride is difficult. A weaker overtone band occurs at 4.84 μm[1] and is frequently used for quantitative analysis[2]. Even though titanium tetrachloride has no significant absorption in this region, the 4.84 μm band is not especially sensitive. Also, carbonyl sulfide absorbs at 4.89 μm[1] and therefore interferes.

A simple wet chemical method for determining vanadium in titanium tetrachloride involves hydrolysis with sulfuric acid and subsequent evaporation of the solution in the presence of nitric acid[3,4]. Vanadium imparts a yellow color to the resulting solution. The evaporation step makes this method somewhat time-consuming and the resulting solutions were found to be difficult to handle because of their high viscosity.

Transition metal chlorides and oxychlorides form colored complexes with many organic compounds. A particularly simple method for determining vanadium oxytrichloride requires only the mixing of equal portions of the titanium tetrachloride sample with thiophene-free benzene[5]. The resulting yellow-orange solution can be measured spectrophotometrically. However, titanium tetrachloride reacts with benzene to form an intensely colored yellow blank. This reduces the accuracy of the method.

Several redox indicators have been reported to respond to oxidizing agents such as vanadium(V) with a high degree of sensitivity. The sensitivity of one such indicator, diphenylbenzidine, relative to the methods mentioned so far is compared in terms of the absorbance produced by 10 p.p.m. vanadium(V) in Table I. The superior sensitivity of the redox indicator is clearly evident. The details of the procedure in which this indicator was employed are discussed below.

Choice of acids for dissolving titanium tetrachloride

When a redox indicator is used for the wet chemical determination of vanadium(V), the complete dissolution of the anhydrous titanium tetrachloride sample is essential. This must be done in concentrated acid solution to prevent the precipitation of hydrous titanium dioxide. Concentrated phosphoric acid cannot be used because of the formation of insoluble titanium phosphates. Concentrated nitric acid is unaccept-

TABLE I

COMPARISON OF SIMPLE SPECTROPHOTOMETRIC METHODS FOR DETERMINING $VOCl_3$ IN $TiCl_4$

Method	*Wavelength*	*Cell path (cm)*	*$TiCl_4$ (ml)*	*Final soln. vol. (ml)*	*Absorbance produced by 10 p.p.m.[d] V*
I.r.	4.84 μm	10.0			0.01
H_2SO_4[a]	445 nm	0.5	10	50	0.02
Benzene[b]	480 nm	1.0	25	50	0.05
Diphenylbenzidine[c]	575 nm	~1.0	10	100	0.54

[a] Data taken from ref. 4.
[b] Use of 10 ml of $TiCl_4$ and 10 ml of benzene gives a more linear calibration curve.
[c] Data obtained by the low-temperature procedure.
[d] Concentration relative to $TiCl_4$ by weight.

able, since its oxidizing character tends to destroy redox indicators. Glacial acetic acid gave highly colored blanks and also prevented the normal color of the oxidized redox indicator from developing.

The solutions which resulted from the use of concentrated sulfuric acid were considered too viscous to work with conveniently. Furthermore, dilution of such solutions liberates a great deal of heat which can be hazardous and which can cause the reduction of vanadium(V) in the presence of chloride. Perchloric acid (70%) was a good solvent but its use caused the color of the oxidized redox indicator to fade immediately after its formation.

Titanium tetrachloride was found to dissolve easily in concentrated hydrochloric acid at a ratio as low as about 1:1.5 by volume. This is a relatively non-hazardous acid to use and the color stability of the indicators was best in this medium. Because of these advantages, hydrochloric acid was chosen as the best acid for dissolving titanium tetrachloride.

Choice of reagent

Two redox indicators that have been reported as reagents for vanadium(V) are 3,3′-dimethylnaphthidine[6,7], and N,N′-diphenylbenzidine[8]. The testing of reagents centered around these compounds and commercially available amine compounds similar to them. Initial tests as to color stability and sensitivity narrowed the field to four compounds: 3,3′-dimethylbenzidine (*o*-tolidine), 3,3′-dimethoxybenzidine (di-*o*-anisidine), N,N′-diphenylbenzidine, and 3,3′-dimethylnaphthidine. The reagents which were eliminated included diphenylamine, sodium *p*-diphenylaminesulfonate, sodium diphenylbenzidinesulfonate, N,N-dimethyl-*p*-phenylenediamine monohydrochloride, N-phenylanthranilic acid, and N-(*p*-methoxyphenyl)-*p*-phenylenediamine monohydrochloride (variamine blue).

Color stability

Figure 1 shows how the more promising redox indicators compare with each other in terms of color stability and sensitivity. Each of the curves was produced with a concentration of 6.50 p.p.m. vanadium as ammonium metavanadate based on the weight of 10 ml of titanium tetrachloride or 112 μg of vanadium for the final solution volume of 100 ml. The procedure used will be described in more detail later.

Dimethylbenzidine is oxidized to a yellow colored compound by vanadium(V), with a wavelength of maximum absorbance of 440 nm. This reagent has a relatively low sensitivity. The oxidized form of dimethoxybenzidine is red-orange with a wavelength of maximum absorbance at 455 nm. This indicator behaves very much like dimethylbenzidine as far as color development and sensitivity are concerned. Oxidation of dimethylnaphthidine gives rise to a red-violet colored compound with maximum absorbance at 555 nm. It is a highly sensitive reagent.

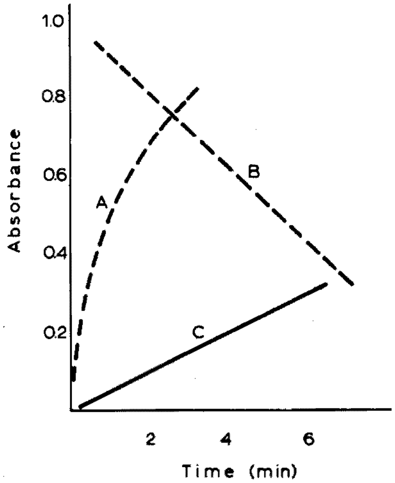

Fig. 1. Color stability of redox indicators. (A) 3,3'-Dimethylnaphthidine; (B) N,N'-diphenylbenzidine; (C) 3,3'-dimethylbenzidine.

The oxidation product of diphenylbenzidine is violet colored (575 nm). Unlike the other three indicators, the color develops immediately and then fades. Immediate color development was considered desirable for possible automation of the analysis. Further, the degree of fading was found to be reproducible. Diphenylbenzidine was chosen as the reagent for determining vanadium(V) because of its advantages of rapid color development and high sensitivity. Also, diphenylbenzidine costs much less than dimethylnaphthidine, the only other indicator tested with comparable sensitivity.

Diphenylbenzidine is not very soluble in most solvents including ethanol. However, 95% ethanol was chosen as the reagent solvent because it did not appear to interfere with the color development. Several concentrations of diphenylbenzidine in 95% ethanol were tested to determine the effect on color intensity. No advantages were found in using a concentration other than a solution saturated at room temperature which is slightly less than 0.1 g l^{-1}.

Effect of acid concentration on color development

Tests were made to determine the optimal volume of concentrated hydrochloric acid needed to hydrolyze 10 ml of titanium tetrachloride while at the same time producing a final acid concentration in 100 ml which would allow immediate and maximum color development; 20 ml was the optimal volume. Other volumes gave less color.

EXPERIMENTAL

The general procedure which was developed and used with ammonium metavanadate as the source of vanadium was as follows.

Place 10 ml of the titanium tetrachloride sample into a dry 100-ml volumetric flask. Add 20 ml of concentrated hydrochloric acid in 5-ml portions down the side of the neck of the volumetric flask. Wait 5 min between the first two additions of acid. After the hydrolysis is complete, add to the flask a total of 30 ml of water containing convenient volumes of vanadium standard. Cool the solution to 25°. Add 10 ml of a saturated solution of diphenylbenzidine in 95% ethanol. Continuously swirl the contents of the flask during the addition. Immediately dilute the solution to 100 ml and thoroughly mix. Using a 0.5-in diameter test tube, measure the absorption at 575 nm with a Bausch and Lomb Model 20 spectrophotometer. The amount of time elapsed between the start of the addition of the redox indicator and the measurement of the color must be closely controlled. A time lapse of 1.5 min was used here.

Precision study

The precision of the above procedure was examined by adding varying amounts (1–10 p.p.m.) of ammonium metavanadate to the solutions. The additions were made just after 10-ml samples of pure titanium tetrachloride had been hydrolyzed by hydrochloric acid. The results (Table II) show an average deviation of 0.2 p.p.m. The precision is quite good considering the color-fading phenomenon. The data fit the equation, p.p.m. vanadium = (13.26) (absorbance) + (0.68), with an average deviation, calculated in terms of p.p.m. vanadium, of 0.05.

TABLE II

PRECISION STUDY

(7–10 determinations were done at each level)

V taken (p.p.m.)[a]	*Absorbance*	*Av. dev. (p.p.m.)*
1.62	0.076	0.13
3.25	0.194	0.18
4.87	0.310	0.22
6.50	0.432	0.15
8.12	0.561	0.25
9.74	0.688	0.34

[a] Relative to the weight of 10 ml of $TiCl_4$.

Low-temperature procedure

After the success with metavanadate standards, titanium tetrachloride solutions of vanadium oxytrichloride were analyzed. It was found that the above procedure would have to be modified to affect the quantitative recovery of vanadium(V) present as vanadium oxytrichloride. A source of error was attributed to the reduction of vanadium(V) during the hydrolysis of the titanium tetrachloride.

Two modifications in the procedure were necessary. One was to reduce the temperature of the solutions before the room-temperature development of the color. The second was to decrease the volume of concentrated hydrochloric acid to 10 ml.

The reason for this is that the acid fumes normally liberated during the "room-temperature" hydrolysis are not evolved at the lower temperature.

The low-temperature procedure was as follows.

Freeze 10 ml of the titanium tetrachloride sample in a dry 100-ml volumetric flask. This can be done with a dry-ice jacket. *Slowly* add 10 ml of concentrated hydrochloric acid pre-cooled to $-25°$ in two 5-ml portions and allow each to freeze separately on top of the frozen titanium tetrachloride. *Very slowly* add 20 ml of water at 0° in four 5-ml portions. Allow each portion to freeze separately on the frozen acid. Add an additional 20 ml water at 0° and allow the sample to thaw gradually at room temperature. Adjust the temperature of the sample to 25°. Immediately add 10 ml of the diphenylbenzidine reagent. Dilute to 100 ml, mix, and measure the color at 575 nm, 1.5 min after the start of the addition of the diphenylbenzidine reagent.

Electron spin resonance examination of the hydrolysis of vanadium oxytrichloride

The two procedures which have been described were compared with a titanium tetrachloride sample containing 10 p.p.m. vanadium as vanadium oxytrichloride. The amount of vanadium(IV) produced in each case was measured by electron spin resonance. A Varian E-3 instrument was used along with the general methodology described in the literature[9,10]. Standards were prepared with pure titanium tetrachloride and vanadium oxydichloride as a source of vanadium(IV). Use of the general testing procedure resulted in reduction of 90% of the vanadium while only 20% was reduced when the low-temperature procedure was followed.

It is believed that the major portion of the vanadium reduction takes place during the hydrolysis step in which water is added following the addition of hydrochloric acid. A temperature of about 60° is reached during this step in the general testing procedure which is the highest temperature the solution reaches during the procedure. Since it was not desired to complicate the procedure further, no step was included in it for oxidizing vanadium(IV) to vanadium(V). Instead the calibration curve was prepared in such a manner as to compensate for any vanadium reduction.

Preparation of a calibration curve

A spectrophotometric calibration curve was prepared with measured volumes of vanadium oxytrichloride in titanium tetrachloride. Eighteen experimental determinations were made at 9 different vanadium levels in the 1–16 p.p.m. range. The equation which best fitted the results was: p.p.m. vanadium = (17.20) (absorbance) + (0.63). The fit of the data to the equation is represented by an average deviation calculated as 0.35 p.p.m. vanadium.

Interferences

Oxidizing agents such as iron(III) chloride, chlorine, and chromyl chloride cause a positive interference.

SUMMARY

A simple method is described for determining vanadium(V) as vanadium oxytrichloride in titanium tetrachloride after dissolution in hydrochloric acid. In this system diphenylbenzidine is oxidized by vanadium(V) to produce a violet colored solution. Spectrophotometric measurements are made at 575 nm. The procedure is designed for the measurement of vanadium in titanium tetrachloride at the 2–10 p.p.m. level.

RÉSUMÉ

Une méthode simple est décrite pour le dosage du vanadium(V) comme oxytrichlorure de vanadium, dans le tétrachlorure de titane, après dissolution dans l'acide chlorhydrique. Dans ce système, la diphénylbenzidine est oxydée par le vanadium(V) en donnant une coloration violette. Les mesures spectrophotométriques sont effectuées à 575 nm. Ce procédé convient au dosage du vanadium dans le tétrachlorure de silicium à des concentrations de l'ordre 2 à 10 p.p.m.

ZUSAMMENFASSUNG

Es wird eine einfache Methode zur Bestimmung von Vanadinoxidtrichlorid in Titantetrachlorid nach Auflösung in Salzsäure beschrieben. In diesem System wird Diphenylbenzidin durch Vanadin(V) oxidiert und ergibt eine violett gefärbte Lösung. Spektrophotometrische Messungen werden bei 575 nm ausgeführt. Das Verfahren eignet sich für die Bestimmung von Vanadin in Titantetrachlorid bei Gehalten von 2–10 p.p.m.

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ETUDE CRITIQUE DU COEFFICIENT D'EXTINCTION DU FER(III) EN MILIEU SULFURIQUE

INFLUENCE DE LA TEMPÉRATURE

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La solution 10^{-3} mol l^{-1} de sulfate ferreux dans l'acide sulfurique 0.4 mol l^{-1} est fréquemment utilisée comme dosimètre chimique des radiations ionisantes[1]. La radiolyse de l'eau produit en effet des espèces oxydantes telles que H_2O_2, HO_2, OH, susceptibles d'oxyder Fe(II) en Fe(III). Or, le sulfate ferrique présente deux bandes d'absorption dans l'ultra-violet (Fig. 1) ce qui permet de le doser par spectrophotométrie. La connaissance du rendement de l'oxydation sous l'effet des radiations permet alors la détermination de la dose.

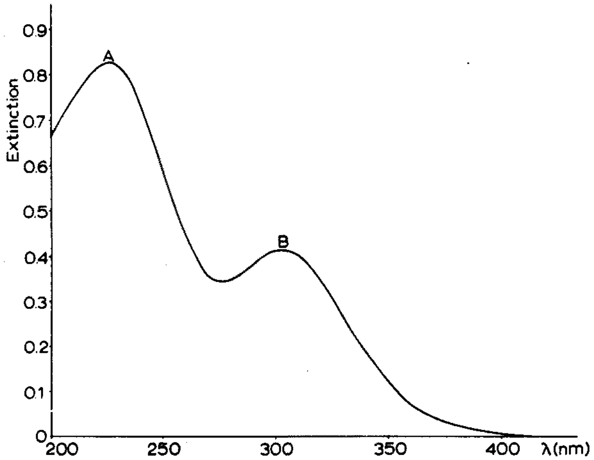

Fig. 1. Spectre optique du sulfate ferrique (milieu acide sulfurique 0.4 mol l^{-1}).

Ce système connu sous le nom de dosimètre de Fricke permet dans une mise en oeuvre courante la détermination de doses allant de 5 à 40 krad avec une précision de quelques pourcents. Deux des facteurs dont dépend cette précision relèvent de la métrologie: le rendement radiochimique (facteur *G*) et le coefficient d'extinction du fer(III) à la longueur d'onde où se fait le dosage spectrophotométrique.

Le facteur *G* a été déterminé avec précision pour divers rayonnements par des

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méthodes calorimétriques notamment[2]. Quant au coefficient d'extinction, sa valeur à 303 nm (longueur d'onde la plus utilisée pour la spectrophotométrie de fer(III)) a été déterminée par de nombreux auteurs mais on observe entre les valeurs présentées des écarts atteignant 4%: (une revue des résultats figure dans les références 3 et 4).

Lors d'une large discussion dans le cadre du symposium organisé par l'AIEA à Vienne en 1966[4], il est apparu que ces divergences quant aux valeurs de ε ne s'expliquaient pas et constituaient un handicap dans certaines applications biologiques et médicales.

Dans ce travail on s'est efforcé de déterminer les causes de ces divergences en étudiant systématiquement les conditions de l'établissement de la courbe d'étalonnage du spectrophotomètre utilisé. Un soin particulier est apporté à la préparation des solutions étalon et à leur contrôle. Les erreurs expérimentales et statistiques sont analysées. On a aussi étudié l'influence de la température sur le coefficient d'extinction.

PARTIE EXPÉRIMENTALE

Les solutions de sulfate ferrique dans l'acide sulfurique 0.4 mol l^{-1} sont préparées par dissolution de fer réduit par l'hydrogène (qualité pour analyse, marque U.C.B.) dans l'acide sulfurique (p.a.; Merck) suivie d'oxydation par H_2O_2 à 30% (p.a.; Merck), la fin de celle-ci étant contrôlée par l,α,α'-dipyridyle (Merck). Après dissolution du fer, les solutions sont filtrées sur creuset filtrant G 4.

Une solution ayant été préparée avec l'acide sulfurique de marque Baker, aucune différence n'a été observée.

Aucun réactif n'a subi de purification ultérieure. L'eau utilisée est une eau déminéralisée distillée ensuite deux fois, respectivement sur $KMnO_4$ acide et sur $Ba(OH)_2$; sa conductivité est celle de l'eau d'équilibre: environ 1 microsiemens.

On prépare d'abord une solution 0.1 mol l^{-1} de fer(III) dans l'acide sulfurique 0.4 mol l^{-1} dont le titre est vérifié par titrage potentiométrique à l'EDTA[5] qui est lui-même titré par le zinc[6]. Le titrage à l'EDTA s'effectue à pH compris entre 2.5 et 3 (ajusté avec sodium hydrogènecarbonate). La stabilité de la lecture est améliorée en faisant barboter CO_2 dans la solution à débit constant ($\pm$0.5 l min^{-1})[7,8]. La potentiométrie est effectuée au moyen d'un pH mètre Beckman Research.

La solution originelle ainsi préparée et titrée est ensuite diluée 250 fois avec l'acide sulfurique 0.4 mol l^{-1} en deux étapes (25 fois et 10 fois) au moyen de pipettes et flacons jaugés contrôlés.

Cette dilution amène à la concentration correspondant au maximum utilisable en spectrophotométrie directe; les autres points s'obtiennent par dilutions et mélanges moitié–moitié, procédé entraînant le minimum d'erreur si l'on emploie le même récipient jaugé pour le prélèvement des deux constituants du mélange.

Les mesures spectrophotométriques sont réalisées au moyen d'un spectrophotomètre Jobin et Yvon, type Maroc II, équipé d'un dispositif de thermostatisation à $\pm 0.1°$ et préalablement étalonné en longueur d'onde avec une lampe à vapeur de mercure.

Ces mesures sont faites par rapport à des solutions de référence (blancs) constituées par le solvant: l'acide sulfurique 0.4 mol l^{-1}.

Les cuvettes en verre de silice sont nettoyées au mélange sulfonitrique ou avec un détergent (Extran, Merck), rincées successivement à l'eau distillée, à l'alcool, à l'éther et séchées. Elles sont toujours employées dans le même ordre et présentent toujours la même face au faisceau incident. Avant la mesure les cuvettes sont remplies de solvant et mesurées les unes par rapport aux autres; si un léger écart est encore observé, la correction correspondante est apportée à la lecture.

Les mesures spectrophotométriques pour la détermination du coefficient d'extinction sont faites à 25°, température contrôlée au sein même des cuvettes au moyen d'une sonde à thermistor de faibles dimensions raccordée à un galvanomètre de marque Ellab.

RÉSULTATS

Titres des solutions originelles de fer(III) dans l'acide sulfurique 0.4 mol l^{-1}

En tenant compte de tous les facteurs d'inexactitude, erreurs systématiques sur les pesées, les contenances des fioles jaugées, des pipettes et des burettes (contrôlées par les fabricants ou étalonnées par nous), on arrive à une évaluation correcte du titre.

Un calcul de propagation des erreurs statistiques déterminées à partir de séries de mesures conduit, par ailleurs, à une évaluation de l'erreur sur ce titre.

On trouve ainsi pour les deux solutions originelles préparées séparément les titres respectifs suivants:

solution I : 0.09050 ± 0.00013 mol l^{-1}
solution II: 0.09961 ± 0.00020 mol l^{-1}

Chacune de ces valeurs résulte de 15 titrages. Les erreurs mentionnées représentent les écarts types sur les moyennes, multipliés par le facteur qui leur donne une signification statistique de 95%.

Concentrations des solutions échelonnées pour l'établissement expérimental de la droite de Lambert–Beer

A partir de la première solution originelle (I), on a préparé quatre séries (I_1, I_2, I_3, I_4) de 9 solutions échelonnées dont les concentrations vont de $(0.2262 \pm 0.0008)\ 10^{-4}$ mol l^{-1} à $(3.6220 \pm 0.0120)\ 10^{-4}$ mol l^{-1}.

A partir de la seconde solution originelle (II) on a préparé 3 séries (II_1, II_2, II_3) de solutions échelonnées comportant respectivement 9, 16 et 16 échantillons. Les concentrations extrêmes de ces séries sont

II_1: $(0.2471 \pm 0.0008)\ 10^{-4}$ et $(3.9543 \pm 0.0130)\ 10^{-4}$ mol l^{-1},
II_2: $(0.2471 \pm 0.0008)\ 10^{-4}$ et $(3.9543 \pm 0.0130)\ 10^{-4}$ mol l^{-1},
II_3: $(0.2474 \pm 0.0008)\ 10^{-4}$ et $(3.9584 \pm 0.0130)\ 10^{-4}$ mol l^{-1}.

Résultats des mesures spectrophotométriques effectuées à 303 nm et à 25°

Les séries I_1, I_2, I_3 et I_4 ont été mesurées deux fois à un jour d'intervalle chacune, sauf la dernière.

Les séries II_1, II_2, II_3 ont été mesurées cinq fois chacune dans un intervalle de temps d'une quinzaine de jours.

Le Tableau I présente les résultats des mesures des séries I; au Tableau II figurent ceux des séries II. Chaque valeur figurant dans ces Tableaux est la moyenne de 5 lectures. Il est à remarquer que les écarts entre les valeurs d'une même solution au cours du temps ne sont pas systématiques.

TABLEAU I

RÉSULTATS DES MESURES D'EXTINCTION À DIFFÉRENTES CONCENTRATIONS (C_i). SÉRIES I

$C_i \cdot 10^4$ (mol l^{-1})	I_1		I_2		I_3		I_4
	1	2	1	2	1	2	1
0.2262	0.0510	0.0540	0.0538	0.0582	0.0570	0.0586	0.0576
0.4525	0.1050	0.1060	0.1068	0.1125	0.1070	0.1088	0.1079
0.9055	0.2066	0.2080	0.2068	0.2124	0.2122	0.2090	0.2096
1.3570	0.3116	0.3132	0.3116	0.3190	0.3123	0.3164	0.3114
1.8110	0.4121	0.4144	0.4140	0.4200	0.4190	0.4140	0.4114
2.2620	0.5139	0.5154	0.5138	0.5210	0.5146	0.5160	0.5134
2.7150	0.6162	0.6174	0.6154	0.6202	0.6180	0.6200	0.6179
3.1670	0.7196	0.7224	0.7130	0.7218	0.7186	0.7176	0.7136
3.6220	0.8120	0.8162	0.8134	0.8212	0.8148	0.8184	0.8142

TABLEAU II

RÉSULTATS DES MESURES D'EXTINCTION À DIFFÉRENTES CONCENTRATIONS (C_i). SÉRIES II

$C_i \cdot 10^4$ (mol l^{-1})	1	2	3	4	5
Série II_1					
0.24715	0.0668	0.0671	0.0634	0.0664	0.0659
0.49429	0.1174	0.1177	0.1170	0.1101	0.1171
0.98859	0.2292	0.2322	0.2279	0.2344	0.2303
1.48588	0.3485	0.3490	0.3480	0.3484	0.3496
1.97717	0.4508	0.4494	0.4529	0.4517	0.4508
2.47147	0.5611	0.5620	0.5588	0.5664	0.5589
2.96576	0.6636	0.6696	0.6681	0.6679	0.6692
3.46005	0.7800	0.7863	0.7866	0.7828	0.7804
3.95435	0.8872	0.8913	0.8933	0.9020	0.8916
Série II_2					
0.24715	0.0582	0.0573	0.0551	0.0616	0.0583
0.49429	0.1146	0.1151	0.1151	0.1184	0.1117
0.74144	0.1682	0.1682	0.1739	0.1742	0.1771
0.98859	0.2248	0.2250	0.2226	0.2298	0.2220
1.23573	0.2805	0.2836	0.2810	0.2868	0.2822
1.48288	0.3404	0.3391	0.3390	0.3424	0.3406
1.73002	0.3914	0.3937	0.3952	0.3978	0.3949
1.97717	0.4513	0.4503	0.4517	0.4489	0.4464
2.22431	0.4965	0.5031	0.5068	0.5087	0.5063
2.47147	0.5570	0.5667	0.5607	0.5602	0.5577
2.71861	0.6182	0.6120	0.6151	0.6148	0.6154
2.96576	0.6742	0.6708	0.6694	0.6688	0.6743
3.21290	0.7214	0.7290	0.7191	0.7203	0.7181
3.46005	0.7804	0.7710	0.7772	0.7775	0.7780
3.70720	0.8277	0.8235	0.8324	0.8441	0.8278
3.95435	0.8841	0.8915	0.9000	0.8922	0.8842
Série II_3					
0.24740	0.0510	0.0536	0.0546	0.0731	0.0630
0.49480	0.1232	0.1232	0.1274	0.1248	0.1247
0.74220	0.1760	0.1741	0.1756	0.2104	0.1717
0.98961	0.2300	0.2230	0.2317	0.2224	0.2306
1.23701	0.2876	0.2860	0.2940	0.2791	0.2869
1.48441	0.3424	0.3350	0.3420	0.3450	0.3446
1.73181	0.4002	0.3947	0.4020	0.4059	0.3980
1.97921	0.4568	0.4537	0.4560	0.4594	0.4558
2.22661	0.5184	0.5117	0.5153	0.5120	0.5137
2.47401	0.5648	0.5698	0.5713	0.5700	0.5665
2.72141	0.6188	0.6216	0.6252	0.6276	0.6192
2.96881	0.6790	0.6774	0.6809	0.6795	0.6782
3.21622	0.7340	0.7295	0.7310	0.7375	0.7331
3.46362	0.7880	0.7849	0.7880	0.7895	0.7860
3.71102	0.8520	0.8404	0.8439	0.8495	0.8458
3.95842	0.9020	0.8922	0.8932	0.8950	0.9036

Calcul des valeurs de ε

On applique la méthode des moindres carrés pour chacun des 22 groupes de mesures afin de rechercher des droites d'équation générale: $E=\varepsilon C+b$. Ceci permet de tirer, outre ε (coefficient angulaire) la valeur d'une éventuelle ordonnée à l'origine (b).

Le Tableau III donne les 22 valeurs trouvées pour ε et b. Pour chacun des 22 ε ainsi calculés par la méthode des moindres carrés, on peut déterminer un écart type σ_ε.

On calcule alors les ε moyens pour chaque série de mesures, chacun d'eux étant donné avec son écart type par l'expression:

$$\varepsilon=(\Sigma\varepsilon_i)/n\pm(\Sigma\sigma_i^2)^{\frac{1}{2}}/n$$

TABLEAU III

VALEURS DES COEFFICIENTS D'EXTINCTION ET DES ORDONNÉES À L'ORIGINE DES 22 GROUPES DE MESURES

Série	*No.*	ε	b	σ_ε
I_1	1	2250	0.0034	9.99
	2	2254	0.0048	8.05
I_2	1	2238	0.0057	7.21
	2	2250	0.0107	7.65
I_3	1	2239	0.0082	8.74
	2	2242	0.0083	6.58
I_4	1	2233	0.0076	5.53
II_1	1	2215	0.0120	11.09
	2	2229	0.0114	9.65
	3	2239	0.0085	10.63
	4	2242	0.0100	12.91
	5	2225	0.0110	10.54
II_2	1	2233	0.0053	8.46
	2	2232	0.0061	10.72
	3	2245	0.0043	8.65
	4	2231	0.0091	6.94
	5	2226	0.0070	9.05
II_3	1	2263	0.0075	8.39
	2	2255	0.0052	9.69
	3	2239	0.0131	7.65
	4	2230	0.0173	13.60
	5	2255	0.0084	5.65

TABLEAU IV

COEFFICIENTS D'EXTINCTION ET ÉCARTS TYPES DES SÉRIES DE MESURES

Série	ε *($l\ mol^{-1}\ cm^{-1}$)*	σ
I_1	2252	6.41
I_2	2242	5.25
I_3	2241	5.47
I_4	2233	5.53
II_1	2230	4.93
II_2	2233	3.95
II_3	2248	4.25

On obtient ainsi les 7 valeurs reprises au Tableau IV. Ces 7 valeurs sont alors combinées pour donner le ε moyen final suivant l'expression

$$\varepsilon_{\text{final}} = \Sigma k_i \varepsilon_i / \Sigma k_i \quad \text{où} \quad k_i = n_i/\sigma_i^2$$

avec

$$\sigma_{\text{final}} = (\Sigma k_i^2 \cdot \sigma_i^2)^{\frac{1}{2}} / \Sigma k_i$$

On trouve finalement pour le coefficient d'extinction à 303 nm et 25°, la valeur:

$$\varepsilon = (2239 \pm 2)\ \text{l mol}^{-1}\ \text{cm}^{-1}$$

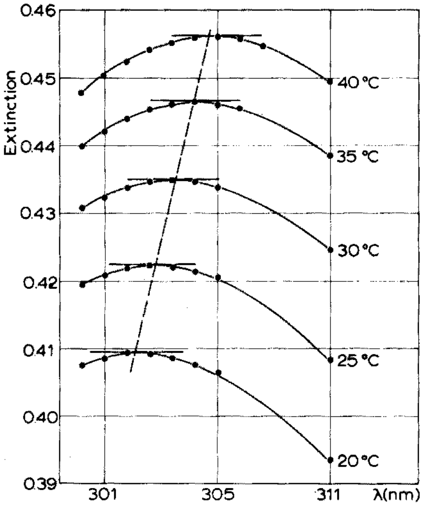
avec une ordonnée à l'origine (moyenne arithmétique des b de chaque droite)

$$b = 0.0084$$

Influence de la température sur le coefficient d'extinction

Les mesures ont été effectuées sur une solution obtenue en diluant 500 fois la solution originelle de fer(III) et par rapport au solvant, l'acide sulfurique 0.8 N. On a travaillé aux températures suivantes: 20, 25, 30, 35, 40°. A chacune de ces températures, on a relevé une partie du spectre (de 300 à 311 nm) et cette opération a été répétée cinq fois à un jour d'intervalle.

Les moyennes à chaque température et à chaque longueur d'onde des cinq séries de mesures sont portées en graphique à la Fig. 2.



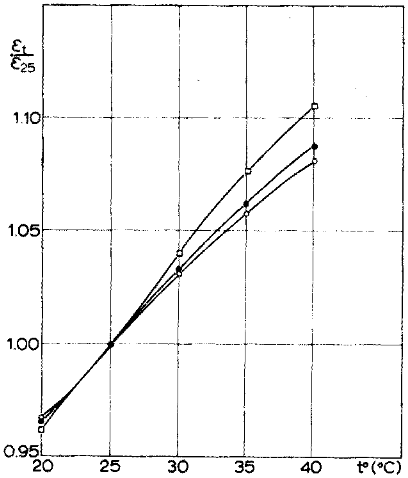


Fig. 2. Influence de la température sur la bande de 303 nm.

Fig. 3. Influence de la température sur ε_{303}. (□) 311 nm, (●) 305 nm, (○) 303 nm.

Il est nécessaire de tenir compte de la dilatation des solutions sous l'effet de la température qui entraîne une certaine dilution et, par conséquent, une erreur par défaut sur les extinctions lues. La formule de correction est la suivante:

$$E_t = E_{\text{lue}}\ (d_4^{25}/d_4^t)$$

où E_t est l'extinction à la température t, normalisée quant au volume, E_{lue}, l'extinction lue à cette température, d_4^{25}, la densité de la solution à 25°, d_4^t, la densité de la solution à la température t.

Les densités de l'acide sulfurique 0.4 mol l^{-1} ont été mesurées aux températures en jeu ici; elles sont données au Tableau V.

Les extinctions aux différentes températures, corrigées pour la variation de densité, peuvent être rapportées à l'extinction à 25° ce qui fournit le rapport des coefficients d'extinction:

$$(E_t/E_{25}) = (\varepsilon_t/\varepsilon_{25})$$

Ces rapports calculés pour trois longueurs d'onde: 303, 305 et 311 nm sont présentés au Tableau VI et portés en graphique à la Fig. 3. On voit qu'entre 20 et 30°, l'effet est à peu près linéaire. A 303 nm, par exemple, l'accroissement du coefficient d'extinction entre 20 et 30° est de 0.66% par degré; il est de 0.69% par degré à 305 nm.

TABLEAU V

DENSITÉ DES SOLUTIONS EN FONCTION DE LA TEMPÉRATURE

Température (°)	d_4^t
20	1.0234
25	1.0218
30	1.0201
35	1.0183
40	1.0162

TABLEAU VI

FACTEURS DE CORRECTION DES COEFFICIENTS D'EXTINCTION POUR L'EFFET DE TEMPÉRATURE

Température (°)	$\varepsilon_t/\varepsilon_{25}$		
	à 303 nm	*à 305 nm*	*à 311 nm*
20	0.967	0.966	0.962
25	1.000	1.000	1.000
30	1.031	1.033	1.041
35	1.058	1.063	1.077
40	1.081	1.088	1.106

DISCUSSION

Détermination du coefficient d'extinction

La valeur trouvée de 2239 l mol^{-1} cm^{-1} à 303 nm et 25° correspond aux valeurs les plus élevées reprises dans la littérature[3]. Elle est très voisine de la valeur 2240 trouvée par HOCHANADEL ET GHORMLEY[2], mais s'écarte de 2% de la valeur moyenne généralement adoptée.

Il faut remarquer d'abord que la plupart des auteurs préparent leurs solutions à partir de fer métallique spectroscopiquement pur, ou de composés de fer(III) p.a. qu'ils considèrent comme substance étalon, c'est-à-dire qu'ils n'effectuent aucun contrôle analytique du titre de la solution elle-même. Or il a été constaté au cours du présent travail que l'eau utilisée pouvait déjà donner lieu à une réduction intempestive du fer(III) si elle n'avait pas subi une purification suffisante. Le mode d'oxydation utilisé (H_2O_2, $KMnO_4$, irradiation), par ailleurs, conduit[9] à des valeurs différentes de ε.

Il est donc recommandable de vérifier le titre de la solution étalon, après sa préparation et de le contrôler ensuite régulièrement.

Influence du spectrophotomètre

Il faut insister sur la nécessité pour tout utilisateur du dosimètre de Fricke souhaitant obtenir des résultats précis (de l'ordre du pourcent), de déterminer ε au moyen du spectrophotomètre qui sera utilisé pour l'analyse des solutions irradiées. La valeur de ε trouvée dans ce travail, il faut le répéter, a été obtenue avec un spectrophotomètre Jobin et Yvon, type Maroc II.

Il semble en effet que chaque valeur de ε obtenue dépende de l'appareil utilisé. Le fait est d'ailleurs signalé par certains auteurs (op. cit.[4])[10].

Ceci explique la divergence des valeurs obtenues avec soin par les différents auteurs. On ne peut donc pas encore avancer une valeur intrinsèque de ce coefficient d'extinction, ce qui implique pour chaque utilisateur la nécessité de le déterminer au moyen du spectrophotomètre qui sera utilisé pour l'analyse des solutions irradiées. Il ne peut être question d'utiliser telles quelles les valeurs trouvées dans la bibliographie, ni leur moyenne, si exactitude et précision sont requises.

Extinction à l'origine

On constate l'existence d'une faible ordonnée à l'origine de la droite de Lambert–Beer. Cette donnée numérique doit être introduite dans les calculs au même titre que ε. Ne pas en tenir compte aboutirait à commettre des erreurs de l'ordre de quelques %. Cette ordonnée à l'origine qui théoriquement devrait être nulle, apparaît ici comme une réalité expérimentale; elle peut être due soit à une déviation à la loi de Lambert–Beer aux basses concentrations, soit à une déficience du spectrophotomètre.

Influence de la température

La variation du coefficient d'extinction sous l'effet de la température est linéaire dans l'intervalle de 20 à 30°. Elle est positive et vaut 0.66% par degré à 303 nm et 0.69% par degré à 305 nm, ceci en accord avec les valeurs avancées par SHARF ET LEE[3]. Au delà de 30° on observe une déviation à la linéarité.

Il est aussi observé que le maximum de la courbe représentant la densité optique en fonction de la longueur d'onde subit un glissement vers le visible avec l'élévation de la température: effet classique en spectrophotométrie[11]. Comme le suggèrent des expériences utilisant comme solvant de l'eau lourde ou comme complexant de l'acide sélénique, ce glissement est vraisemblablement dû à des altérations dans la nature du complexe fer–sulfate–eau, ce qui entraîne une modification du champ de ligands[12]. Le maximum à 220 nm est également sensible à des variations sous l'action de la température mais celles-ci sont plus faibles (de l'ordre de 0.3% par degré).

Ces observations indiquent la nécessité d'une bonne thermostatisation et d'un contrôle constant de la température, dans la cuvette, si des mesures précises sont désirées.

Conclusion

Ces mesures et ces considérations plaident en faveur de l'utilisation du dosimètre au sulfate ferreux à condition que certaines précautions rigoureuses soient prises quant à l'étalonnage et la thermostatisation du spectrophotomètre. La moindre omission dans ces diverses vérifications peut amener des erreurs atteignant plusieurs pourcents.

RÉSUMÉ

On a déterminé le coefficient d'extinction du fer(III) à 303 nm et 25° en milieu H_2SO_4 0.4 mol l^{-1}. La valeur trouvée est de 2239 ± 2 l mol^{-1} cm^{-1}. L'influence de la température sur le coefficient d'extinction est de 0.66% par degré entre 20 et 30°.

SUMMARY

The molar absorptivity of iron(III) at 303 nm and 25° in 0.4 *M* sulphuric acid has been studied. The value was found to be 2239 ± 2 l mol^{-1} cm^{-1}, and the effect of temperature on the absorptivity was 0.66% per degree between 20 and 30°. These values may vary according to the instrumentation used. Standard solutions must be prepared and standardized with great care and the spectrophotometer cells must be properly thermostated, otherwise errors of several per cent may occur.

ZUSAMMENFASSUNG

Es ist der molare Extinktionskoeffizient von Eisen(III) bei 303 nm und 25° in 0.4 *M* Schwefelsäure bestimmt worden. Er wurde zu 2239 ± 2 l mol^{-1} cm^{-1} ermittelt; der Temperatureinfluss auf den Extinktionskoeffizienten betrug zwischen 20 und 30° 0.66% pro Grad. Diese Werte können je nach verwendeter Apparatur variieren. Die Standardlösungen müssen mit grosser Sorgfalt angesetzt und eingestellt werden. Die Küvetten müssen gut thermostatisiert werden, andernfalls können Fehler von einigen Prozent auftreten.

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THE COULOMETRIC TITRATION OF BARBITURATES*

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Although some recent reviews describe the application of constant-current coulometry to the analysis of organic compounds[1] and pharmaceuticals[2], there are only a few examples of the application of this method to the analysis of barbiturates. In most instances either an unsaturated group or the weakly acidic characteristic of the barbiturate was utilized to perform the titration.

KALINOWSKI AND BARAN[3] employed electrogenerated chlorine to determine cyclohexalbarbitone and hexabarbitone. Chlorine was also the titrant in the titration of diallylbarbitone[4]. CHARLES AND KNEVEL[5] used the reaction between bromine and an allyl group to determine sodium seconal. Since the reaction of this compound with bromine is slow, a back-titration employing standard arsenite was performed. Thiopental sodium has also been determined by titration with coulometrically generated bromine[6].

NIKOLIC AND BLAGOJEVIC[7] have employed constant-current coulometry to titrate both barbituric acids and their sodium salts. The acids were titrated with hydroxide ion generated from a solution of sodium sulfate in 10% ethanol; thymolphthalein served as the indicator. The sodium salts were titrated with hydrogen ion generated from the same electrolyte; *p*-dinitrophenol was the indicator. The results of the coulometric titrations were found to agree well with those obtained by conventional volumetric means.

The present investigation was undertaken as a continuation of the application of coulometric titrations to the analysis of toxic substances[8,9].

EXPERIMENTAL

Apparatus

All coulometric measurements were made with a Microcoulometric Quantalyser Model 6 (ChrisFeld Precision Instruments Inc., Beltsville, Md.). The current output of this instrument was calibrated by measurement of the potential drop across a 100-ohm, 0.1% precision resistor with a Leeds and Northrup 8687 Volt Potentiometer.

The titration cell was made from a weighing bottle with a 2.0-cm inner diameter. Electrogenerated mercury(II) was produced by oxidation of a mercury

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pool. Electrical contact to the mercury pool was made with a small piece of platinum wire sealed into the base of the titration cell. The isolated generator cathode was a piece of platinum wire. The isolation compartment was connected to the titration solution through an agar–potassium nitrate salt bridge. Halide salt bridges were avoided because of the reaction of halides with the generated mercury(I) and mercury-(II). The salt bridge was made according to the directions of MEITES[10], potassium nitrate being substituted for potassium chloride. A small volume of potassium nitrate solution was placed on top of the agar and the platinum-wire cathode made contact with this solution. An isolation compartment constructed of "thirsty glass" (porous Vycor, Corning Glass Works, Corning, N.Y.) held onto the end of a glass tube with a Manolok Teflon Sleeve (Manostat Corp., New York) served equally well in isolating the cathode from the test solution. This latter compartment was actually more desirable since it no longer necessitated replacement of the agar.

The biamperometric end-point detection method was employed with a potential of 150–200 mV imposed across two identical platinum-wire electrodes. The potential across the indicating electrodes was supplied by a Sargent Model XV Polarograph. All biamperometric end-points were determined by recording the changes in current on this polarograph. In all titrations with electrogenerated mercury(II), the end-points were determined by extrapolation of the straight lines before and after the current rise.

Agitation of the titration mixture was accomplished by means of a magnetic stirring bar which floated on top of the mercury pool. The titration cell was water-jacketed so that titrations could be performed at controlled temperatures.

Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer. The KBr disc technique was employed exclusively. In most cases a 1% pellet was made; however, in some instances the concentration in the pellet had to be reduced. The pellet was heated in a drying oven at 115° before the spectrum was taken. If this precaution was not taken, a broad absorption band always appeared in the 3500 cm^{-1} region.

Reagents

All chemicals were reagent grade whenever possible and were used without further purification. The barbiturates were purchased as the sodium salts and were employed without further purification. In studies where the acid form of the barbiturate was desired, it was prepared by adding an aqueous solution of the sodium salt to a dilute solution of nitric acid. The resulting precipitate was collected, washed, and recrystallized from water.

Procedures

Preparation of mercury barbiturate compounds from mercury(II) oxide[11]. The sodium salt of the barbiturate (1 g) was stirred with 4 g of orange mercury(II) oxide, 20 ml of 0.05 *M* sodium carbonate buffer, pH 9.5, and 300 ml of freshly distilled chloroform for several hours. The chloroform layer was then separated in a separatory funnel, filtered, and evaporated to a volume of approximately 20 ml. The mercury–barbiturate compound was then precipitated with several hundred ml of petroleum ether (b.p. 40–60°). The precipitate was collected, washed with petroleum ether, and dried in a vacuum desiccator over phosphorus pentoxide.

Preparation of mercury barbiturate compounds from mercury(II) nitrate. The sodium salt of the barbiturate was dissolved in distilled water and this solution was added to a solution of mercury(II) nitrate acidified with nitric acid. The solution was filtered and the precipitate was washed several times with water and finally with acetone. This method of preparation assured an excess of mercury(II) nitrate.

Preparation of coulometrically generated mercury barbiturate compounds. Approximately 4 ml of 0.67 N potassium nitrate and 1.0 ml of a standard barbiturate solution were added to the titration cell. After each titration, the titration mixture was removed from the cell and stored in a beaker. Several titrations were performed in this manner until a sufficient quantity of precipitate was collected. The precipitate was then filtered on a Millipore filter and washed several times with water. The precipitate was then washed from the Millipore filter with water and the resulting mixture was evaporated to dryness and the crystals collected.

Analysis of compounds for mercury. For the mercury–barbiturate compounds that could be prepared in sufficiently large quantities, the procedure recommended by COHEN[12] was employed. Approximately 100 mg of sample was weighed out and transferred to an Erlenmeyer flask, 6 ml of concentrated nitric acid was added and the solution was heated until oxides of nitrogen were removed. The solution was diluted with *ca.* 25 ml of water, 2 ml of ammonium iron(III) sulfate indicator were added, and the solution was titrated with standard 0.01 M potassium thiocyanate. The potassium thiocyanate was standardized against primary standard silver nitrate.

RESULTS AND DISCUSSION

The results of the titration of sodium phenobarbital (sodium 5-ethyl-5-phenylbarbiturate), sodium barbital (sodium 5,5-diethylbarbiturate), sodium sandoptal (sodium 5-allyl-5-isobutylbarbiturate), and sodium seconal (sodium 5-allyl-5-(1-methylbutyl)barbiturate) in 20% acetone at 37° with coulometrically generated mercury(II) are given in Table I. An inspection of this Table shows that all of the compounds are titrated similarly with the mercury(II); in all cases the mercury(II)–barbiturate ratio is 1:1. This fact is particularly interesting in the case of the allylic barbiturates. With these compounds, addition of the mercury(II) across the double bond is a possible reaction not present with the other compounds. This would result in the consumption of more than one mole of mercury(II). The data clearly show, however, that only one mercury(II) reacts per mole of allylic barbiturate, indicating that the allylic barbiturates react in a manner similar to the other compounds.

The accuracy of these titrations was usually around 5% for barbiturate levels down to *ca.* 75 μg. Below these levels, the accuracy was considerably poorer, primarily because of the error involved in measuring short titration times. The precision was *ca.* 5%, which is reasonably good since the end-point was determined by manual extrapolation of the titration curve.

Effect of titration temperature

The data shown in Table I are for titrations at 37°. Similar data were obtained when the titrations were performed at room temperature. Qualitatively, the titration

TABLE I

COULOMETRIC TITRATION OF BARBITURATES AT 37°

(n: μmoles added per μeq found. Generation current: 0.965 mA. Indicator potential: 150 mV. Current sensitivity: 0.006 μA mm^{-1}. Supporting electrolyte: 0.5 M $NaClO_4$, 20% acetone)

μeq added	*μeq found*	*n*	*μg added*	*μg found*	*Ave*	*% Error*
Sodium phenobarbital						
1.786	1.710	1.05	454.0	435	441 ± 6	3.0
	1.758	1.02		447		
0.8930	0.930	0.96	227.0	236	234 ± 2	3.2
	0.924	0.97		235		
	0.912	0.98		232		
0.4465	0.462	0.96	113.5	117	111 ± 4	2.0
	0.426	1.05		108		
	0.426	1.05		108		
0.1786	0.150	1.19	45.40	38.1	41.2 ± 2	10.0
	0.162	1.10		41.2		
	0.174	1.03		44.2		
Sodium barbital[a]						
3.658	3.324	1.10	754.2	685	699 ± 9	7.3
	3.408	1.05		703		
	3.342	1.07		708		
2.926	2.754	1.06	603.4	568	571 ± 10	5.3
	2.760	1.06		569		
	2.796	1.05		576		
1.463	1.338	1.09	301.7	276	286 ± 4	5.3
	1.434	1.02		296		
0.7318	0.786	0.93	150.8	162	162 ± 1	7.3
	0.780	0.94		161		
	0.792	0.92		163		
0.3658	0.420	0.87	75.42	86.6	87.4 ± 1	16.0
	0.432	0.85		89.1		
	0.420	0.87		86.6		
Sodium sandoptal						
1.935	1.932	1.00	476.4	476	486 ± 10	2.1
	1.992	0.97		491		
	2.004	0.97		494		
0.9777	0.972	1.00	240.7	239	231 ± 6	4.0
	0.906	1.08		223		
	0.936	1.04		230		
0.4860	0.468	1.04	119.6	115	115 ± 2	4.0
	0.456	1.07		112		
	0.474	1.03		117		
0.1930	0.174	1.11	47.62	42.8	45.8 ± 8	3.9
	0.204	0.95		50.2		
	0.180	1.07		44.3		
Sodium seconal						
2.909	2.748	1.06	757.2	715	722 ± 4	4.6
	2.778	1.05		723		
	2.796	1.04		728		
2.327	2.202	1.06	605.8	573	576 ± 5	4.9
	2.224	1.04		584		
	2.196	1.06		572		
1.164	1.116	1.04	302.9	290	300 ± 6	1.1
	1.198	0.97		312		
	1.140	1.02		297		
0.5816	0.558	1.04	151.4	145	145 ± 1	4.1
	0.564	1.03		147		
	0.552	1.05		144		
0.2909	0.216	1.35	75.72	56.2	55.2 ± 1	27.0
	0.210	1.39		54.7		
	0.210	1.39		54.7		

[a] Current sensitivity: 0.003 μA mm^{-1}.

curves were the same at both temperatures, but the end-point was slightly sharper at the higher temperature. Statistical analysis employing the F-Test[13] verified that no significant difference existed in the standard deviations at room temperature and 37°.

To study the effect of lowering the solubility of the mercury–barbiturate precipitate, the temperature of the titration cell was held at 4° with circulating water from an ice bath. The end-points of the titration were very poor and the titration times were higher than theory. Apparently, under these conditions, there was a decrease in the reaction rate in addition to a lowering of the solubility of the precipitate. The results indicate that the reaction rate is the more dominant factor.

Effect of acetone concentration

Preliminary results with sodium phenobarbital showed that the titration of this compound in amounts of 150 μg or less was not possible in an aqueous medium. Since this is a precipitation titration, one of the variables affecting both the precision and accuracy of the titration is the solubility of the mercury–barbiturate compound. Both the precision and accuracy are favored by lowering the solubility of the mercury–barbiturate compound in the titration medium. A 20% acetone medium was studied and was found to be very satisfactory.

The effect of acetone concentration was investigated by increasing the acetone concentration to 50% (v/v). The results of the titration of sodium phenobarbital in 50% acetone are shown in Table II. In general, these results are comparable to those obtained in 20% acetone. However, the precision and accuracy are slightly poorer.

TABLE II

TITRATION OF SODIUM PHENOBARBITAL IN 50% ACETONE

(Supporting electrolyte: 0.3 *M* KNO_3. Other variables were as shown in Table I.)

µeq added	*µeq found*	*n*	*µg added*	*µg found*	*Ave*	*% Error*
0.9943	0.978	1.02	252.8	248	246 ± 3	2.6
	0.966	1.03		246		
	0.960	1.03		244		
0.7022	0.672	1.04	178.5	171	169 ± 2	5.2
	0.672	1.04		171		
	0.674	1.07		166		
0.4972	0.450	1.10	126.4	114	120 ± 4	5.5
	0.468	1.06		119		
	0.492	1.01		125		
0.2944	0.276	1.06	75.22	70.2	73.7 ± 3	2.0
	0.306	0.96		77.8		
	0.288	1.03		73.2		

Large concentrations of acetone can dehydrate the salt bridge, increasing the resistance of the titration cell if an air bubble forms in the dehydrated area. This makes necessary more frequent adjustments of the coulometer balancing circuit;

therefore the current is not always under precise control. Since a precisely controlled current is fundamental to constant-current coulometry, any deviations in the current will cause deviations in the accuracy and precision of the titration. This is apparent in the data, since both the accuracy and precision are poorer than with the titrations performed in 20% acetone.

Effect of supporting electrolyte

The data presented in Table I were obtained with a supporting electrolyte of sodium perchlorate. Potassium nitrate was also employed as the supporting electrolyte, and was found to be equally satisfactory. The qualitative nature of the titration curves was the same, indicating that the titration reaction is the same in both supporting electrolytes.

The electrogeneration of mercury(II)

It is possible to generate both mercury(I) and mercury(II) coulometrically. The normal procedure is to generate mercury(II) in basic solution[14–17] and mercury(I) in acid solution[14,15,18]. Both electrogenerations have been reported to occur with 100% current efficiency.

A typical curve for the coulometric titration of all the barbiturates investigated exhibits an initial rise in the current followed by a decrease to a limiting value. The current then remains constant until the end-point is reached, at which point there is a sharp increase in current.

It is felt that under these conditions mercury(II) is the eventual titrant, although it is not generated directly. Mercury(I) is initially generated and this disproportionates into the element and mercury(II). Mercury(II) forms a more stable complex with the barbiturate than does mercury(I); therefore the disproportionation of mercury(I) is favored. COHEN[12] has observed that the mercury(II) complexes of barbiturates are more stable than the mercury(I) complexes.

The coulometric titration curve is interpreted as follows. The initial increase in current is due to the initial generation of mercury(I) followed by its disproportionation into the element and mercury(II). The indicator cathode is depolarized by the reduction of mercury(I) at its surface and the indicator anode is depolarized by the oxidation of the element to mercury(I). Since both indicator electrodes are depolarized, a current flows. The mercury(II) formed by the disproportionation reacts with the barbiturate to form a stable complex. This enhances the disproportionation of mercury(I), and the current decreases as the amount of mercury(I) decreases until a steady-state concentration of mercury(I) is present. This point is marked by the linear baseline on the titration curve. When all of the barbiturate is consumed, the disproportionation of mercury(I) is reduced, and the current increases owing to the presence of an increased concentration of mercury(I).

Several observations were made to confirm this interpretation of the titration curve. A black substance appears in the coulometric titration cell during the titration; this substance appears to be finely divided mercury formed by the disproportionation of mercury(I). KIES AND VAN WEEZEL[19] have made this same observation during the coulometric titration of thiourea with generated mercury(II). In addition to the above, some qualitative tests were run. The generation was carried out in potassium nitrate medium and some of the solution was collected. Tin(II) chloride was added to one portion of the collected electrolyte and a black precipitate appeared immediately, presumably caused by the reduction of mercury(II) to the element. One drop of hydrochloric acid was added to a second portion of the collected electrolyte and a white precipitate was formed. This precipitate was identified as mercury(I) chloride. Also, when the generation was permitted to take place in the presence of the sodium salt of the barbiturate and the precipitate was collected, filtered, and washed, elemental mercury was actually observed admixed with the precipitate.

All of the above observations strongly suggest that both mercury(I) and mercury(II) species are present, presumably owing to the initial generation of mercury(I) followed by its disproportionation into the element and mercury(II).

The reaction between mercury(II) and sodium phenobarbital

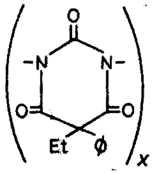
Qualitative and quantitative studies were performed on the product of the reaction between coulometrically generated mercury(II) and sodium phenobarbital. Other workers have investigated the reaction between mercury(II) and barbituric acid derivatives, and several different types of compounds have been reported, depending upon the method of preparation. BJORLING *et al.*[11] have reported a polymeric structure in which the unit cell consists of one molecule of mercury(II) and one molecule of barbiturate. This polymer is formed when the barbiturate is allowed to react with mercury(II) oxide. This same type of compound has been reported when prepared electrolytically by controlled-potential coulometry[12]. BJORLING *et al.*[20] also have reported a compound which contains two molecules of barbiturate for every molecule of mercury(II). This compound is formed if there is substitution on one of the nitrogen atoms in the barbiturate molecule. POETHKE AND FURST[21] have described a compound which shows 1:1 stoichiometry with the second valence of mercury(II) being occupied by a second ligand, for example, hydroxide or acetate ion, depending on the method of synthesis.

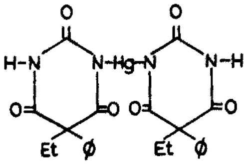
Since a detailed structural elucidation of the reaction between coulometrically generated mercury(II) and the sodium salts of the barbituric acids was outside the scope of this coulometric study, only a few basic characteristics of the compound produced with sodium phenobarbital will be enumerated. In this case fairly definite statements may be made about the structure of the compound formed, while in the other instances the data do not permit one to make definite conclusions about the structure of the compound formed.

The most important observation is that the constant-current coulometric data clearly show the formation of a 1:1 mercury(II)–barbiturate complex. The polymeric mercury–barbiturate compound of BJORLING *et al.*[11] was prepared. Elemental analysis of the polymer agreed reasonably well with theory. An infrared spectrum of this compound was identical with that of the compound isolated from the coulometry cell. The N–H stretch band at 3160 cm^{-1} found in the spectrum of sodium phenobarbital was absent from both these spectra.

It is interesting to note that the polymeric compound is different from the one obtained when sodium phenobarbital is permitted to react with either mercury(II) chloride or mercury(II) nitrate. Apparently two molecules of barbiturate combine with one molecule of mercury(II). Except for the carbon analysis, which was *ca.* 1.3% lower than the theoretical value, the values for this compound agreed well with theory. The infrared spectrum showed that there is a definite N–H stretch in the

3200 cm^{-1} region, indicating that there is a free N–H group in the compound. On the basis of these data, the following structures have been tentatively assigned to the two species.


Polymeric compound


Mercury–phenobarbital prepared from $HgCl_2$

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SUMMARY

Constant-current coulometry has been applied to the titration of barbituric acid derivatives, *i.e.*, sodium phenobarbital, sodium seconal, sodium barbital, and sodium sandoptal. The titrant is generated mercury(II). The titration may be performed in aqueous potassium nitrate–acetone, or aqueous sodium perchlorate–acetone solutions. The most sensitive systems are the partially nonaqueous ones, with both supporting electrolytes giving similar results. Comparable results also were obtained at room temperature and at 37°. Considerable evidence has been obtained to support the theory that mercury(II) is not generated directly in these media, but is formed from the disproportionation of mercury(I) into the element and mercury(II). Qualitative tests proved the presence of all three species in the titration medium. Structural analysis of the compound formed in the coulometry cell was performed, and with sodium phenobarbital the evidence indicates that a polymeric compound containing continuous Hg–N linkages is formed. The evidence for the other compounds is less conclusive, probably because a mixture of products is formed in the titration cell.

RÉSUMÉ

La coulométrie à courant constant est appliquée au titrage de divers dérivés de l'acide barbiturique. Le mercure(II) formé coulométriquement constitue le titrant. Ce dosage peut s'effectuer soit dans une solution nitrate de potassium–eau–acétone, soit dans une solution perchlorate de sodium–eau–acétone. Le mercure(II) n'est pas formé directement dans ce milieu; il résulte de la dismutation du mercure(I) en élément et mercure(II). Des essais qualitatifs ont prouvé la présence de ces 3 formes au cours du titrage. On examine également la structure des composés formés au cours de ce dosage.

ZUSAMMENFASSUNG

Barbitursäurederivate wie Natriumphenobarbital, Natriumseconal, Natriumbarbital und Natriumsandoptal sind mit coulometrisch bei konstantem Strom erzeugtem Quecksilber(II) titriert worden. Die Titration kann in Lösungen von Kaliumnitrat oder Natriumperchlorat in Wasser–Aceton ausgeführt werden. Die teilweise nichtwässrigen Systeme sind die empfindlichsten, wobei beide Trägerelektrolyte zu ähnlichen Ergebnissen führen. Vergleichbare Ergebnisse wurden auch bei Raumtemperatur und bei 37° erhalten. Die Befunde stützen die Annahme, dass Quecksilber(II) in diesen Medien nicht direkt, sondern durch Disproportionierung von Quecksilber(I) in das Element und Quecksilber(II) gebildet wird. Qualitative Proben bewiesen die Anwesenheit aller drei Spezies im Titrationsmedium. Eine Strukturanalyse der bei der Coulometrie gebildeten Verbindungen weist im Falle von Natriumphenobarbital auf eine polymere Verbindung mit fortlaufenden Hg–N-Bindungen hin. Die Befunde bei den anderen Verbindungen sind weniger überzeugend, wahrscheinlich weil ein Gemisch von Substanzen in der Titrationszelle gebildet wird.

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COMPLEXIMETRIC TITRATION OF GALLIUM WITH COPPER–EDTA–TAR AS INDICATOR

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When no appropriate metal indicator is available for the compleximetric titration of a metal M, an alternative NY–HA indicator system[1] should be sought and is sometimes found very useful. Thus for the compleximetric titration of gallium, the CuY–PAN system has been recommended[2]. However, the end-point is sluggish and the situation is not improved much by the use of pyrocatechol violet as an indicator[3]. Because of the slow indicator transition in these titrations, titration should be done very slowly or at boiling temperature.

The present paper describes a method of compleximetric titration of gallium with the Cu–EDTA–TAR system as an indicator. The end-point is sharp, and the method is simple and accurate.

THEORETICAL CONSIDERATIONS

In discussing the indicator transition of a compleximetric titration with an NY–HA system as indicator, the following two cases should be distinguished[1]: (*a*) $K_{\mathrm{N'Y'(NY)'}} > K_{\mathrm{M'Y'(MY)'}}$, *e.g.* the indicator system Mg–EDTA–Erio T in the titration of barium[4], Cu–EDTA–PAN in the titration of aluminum[5] and Zn–EGTA–PAN[6,7] or Zn–EGTA–Zincon[8,9] in the titration of calcium; (*b*) $K_{\mathrm{N'Y'(NY)'}} < K_{\mathrm{M'Y'(MY)'}}$, *e.g.* Mg–EDTA–Erio T in the titration of calcium[4]. Here, the conditional formation constant $K_{\mathrm{M'Y'(MY)'}}$ is defined as:

$$K_{\mathrm{M'Y'(MY)'}} = \frac{[(\mathrm{MY})']}{[\mathrm{M'}][\mathrm{Y'}]}$$

where $[(\mathrm{MY})']$ denotes total concentration of 1:1 MY complexes involving protonated and/or hydroxo complexes, $[\mathrm{M'}]$ total concentration of the metal M not combined with Y and $[\mathrm{Y'}]$ total concentration of unmetallized EDTA.

The indicator system Cu–EDTA–TAR in the titration of gallium corresponds to the latter case, *i.e.* a partial replacement titration. As in the previous paper[1], the following stoichiometric relationships hold:

$$C_{\mathrm{Ga}} = [(\mathrm{GaY})'] + [\mathrm{Ga'}] \qquad (1)$$

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$$C_Y = [(GaY)'] + [(CuY)'] + [Y'] \tag{2}$$

$$C_{Cu} = [(CuY)'] + [Cu'] \tag{3}$$

$$C_A = [(CuA)'] + [(GaA)'] + [A'] \tag{4}$$

where C_{Ga} is the total concentration of gallium, C_Y the total concentration of EDTA, C_{Cu} the total concentration of copper, and C_A the total concentration of TAR.

The formation of GaA being negligible ($C_A = [(CuA)'] + [A']$) in the vicinity of the equivalence point, the transition of the system indicator is given by the following substitution reaction,

$$(CuA)' + Y' \rightleftharpoons (CuY)' + A' \tag{5}$$

with the equilibrium constant

$$K = \frac{[(CuY)'][A']}{[(CuA)'][Y']} = \frac{K_{CuY'(CuY)'}}{K_{CuA'(CuA)'}}$$

By appropriate substitutions and rearrangements of eqns. (1)–(5), we have the following expression for the fraction titrated "a" near the equivalence point:

$$a = 1 - \frac{1-\phi}{\phi}\left(\frac{K_{CuY}C_{Ga}\alpha_{Ga}\alpha_{CuY}}{K_{GaY}C_{Cu}\alpha_{Cu}\alpha_{GaY}} + 1\right)\frac{\alpha_{Cu}\alpha_{A(H)}}{K_{CuA}C_{Ga}\alpha_{CuA}} + \frac{\phi}{1-\phi}\,\frac{K_{CuA}C_{Cu}\alpha_{Y}\alpha_{CuA}}{K_{CuY}C_{Ga}\alpha_{A(H)}\alpha_{CuY}} \tag{6}^*$$

where ϕ refers to the indicator transition defined as $\phi = [A']/C_A$, and α_{Cu}, α_{Ga}, $\alpha_{A(H)}$, α_{CuY}, α_{GaY} and α_{CuA} are the side-reaction coefficients for Cu, Ga, TAR, Cu–EDTA, Ga–EDTA and Cu–TAR, respectively[10]. The second term on the right-hand side of eqn. (6) mainly concerns the indicator transition before the equivalence point and the third term mainly concerns that after the equivalence point.

Let,

$$\left(\frac{K_{CuY}C_{Ga}\alpha_{Ga}\alpha_{CuY}}{K_{GaY}C_{Cu}\alpha_{Cu}\alpha_{GaY}} + 1\right)\frac{\alpha_{Cu}\alpha_{A(H)}}{K_{CuA}C_{Ga}\alpha_{CuA}} = f_1$$

$$\frac{K_{CuA}C_{Cu}\alpha_{Y}\alpha_{CuA}}{K_{CuY}C_{Ga}\alpha_{A(H)}\alpha_{CuY}} = f_2 \tag{7}$$

Then, eqn. (6) simplifies to:

$$a = 1 - \frac{1-\phi}{\phi}f_1 + \frac{\phi}{1-\phi}f_2 \tag{8}$$

The lower f_1 and f_2, the sharper the indicator transition in the vicinity of the equivalence point. As is evident from eqn. (7), both f_1 and f_2 depend on the concentrations of copper and gallium as well as hydrogen ion.

RESULTS AND DISCUSSION

The f_1 and f_2 values calculated for various experimental conditions are given in Table I. It is clear that a sharp and distinct indicator transition can be expected

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* Near the equivalence point $[(CuY)']$ can be approximated as C_{Cu}.

at pH values higher than 3.0 under the conditions given in Table I, *i.e.* both f_1 and f_2 values are so low that the visual titration would be possible under these conditions.

Effect of pH

In Figure 1 are given titration curves near the equivalence point at various pH values. Above pH 3, the indicator transition is very sharp, while below pH 3 it becomes less sharp as the pH decreases. This is just as expected from theoretical considerations[1].

TABLE I

f_1 AND f_2 AT VARIOUS pH VALUES

(Conditions: $C_{Ga} = 10^{-3}\,M$, $C_{CuY} = 10^{-3}\,M$, $C_A = 10^{-5}\,M$)

pH	*log f_1*	*log f_2*
2.0	−1.04	−2.28
2.5	−1.61	−2.87
3.0	−2.14	−3.30
3.5	−2.60	−3.72
4.0	−3.02	−4.01
4.5	−3.35	−4.24
5.0	−3.33	−4.32

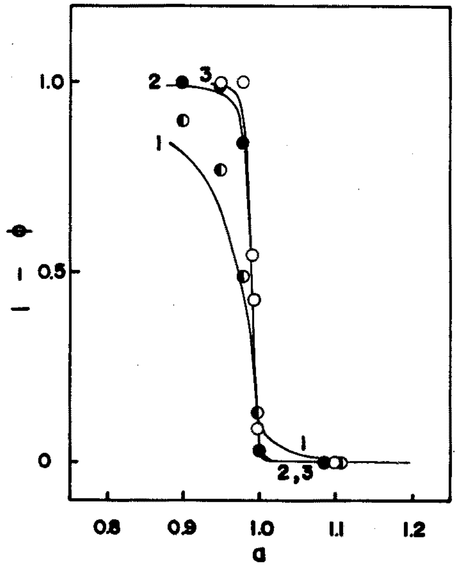

Fig. 1. Effect of pH on the indicator transition. Conditions: $C_{Ga} = 10^{-3}\,M$, $C_{CuY} = 10^{-3}\,M$, $C_{Ga} = 2 \times 10^{-5}\,M$ (—) Theoretical indicator transition: (1) pH 2.58, (2) pH 3.95, (3) pH 4.90. Experimental values: (◐) pH 2.58, (●) pH 3.95, (○) pH 4.90.

Above pH 4, gallium hydroxide precipitates and the aggregate of the hydroxide seems to react slowly with EDTA. Thus at higher pH a more or less premature end-point is observed, especially for the lower concentration of CuY used (see Table II). Recoloration occurs at the premature end-point, when the solution is heated.

TABLE II

INDICATOR TRANSITION UNDER VARIOUS CONDITIONS

C_{CuY}/C_{Ga}[a] pH	0.1	0.2	0.5	1.0	1.5	2.0
3.0	X[b]	X	O	O	O	O
3.5	X	O	O	O	O	O
4.0	O	O	O	O	O	O
4.5	X	X	X	O	O	O
5.0	X	X	X	X	O	O

[a] $C_{Ga} = 10^{-3}$ *M*.
[b] O: Sharp and distinct indicator transition.
X: Premature indicator transition and recoloration on standing.

Effect of Cu-EDTA concentration

For the successful titration of gallium by the present method, it is necessary that equilibria (5) and (9) be favored to the right.

$$Ga' + (CuY)' + A' \rightleftharpoons (GaY)' + (CuA)' \qquad (9)$$

The higher the concentration of CuY, the more favored to the right is the equilibrium (9). However, too high a concentration of CuY makes the visual detection of the end-point difficult, owing to the intense color of CuY.

A high CuY concentration is also desirable from the kinetic point of view. The reaction of gallium ion with EDTA proceeds more slowly than the reaction of CuA with EDTA, thus making the end-point premature in the titration with a low CuY concentration. In the titration with high CuY concentrations, on the other hand, most gallium ions are transformed to GaY, giving rise to an equivalent amount of copper ion, which reacts rapidly with EDTA.

Based on these equilibria and kinetic considerations, one can conclude that the use of 10^{-2} *M* CuY is appropriate for the visual titration of gallium (see also Tables I and II).

Under the optimal conditions given in the recommended procedure, the visual titration of gallium is possible at room temperature, though it is preferable to heat the solution near the end-point in order to be sure that the titration is complete.

Accuracy and precision

In Table III, the results obtained gravimetrically by the 8-hydroxyquinoline

TABLE III

ACCURACY AND PRECISION

Sample no.	*Ga taken (mg/100 ml)*	*Ga found (mg/100 ml)*
1	6.78	6.73 6.74
2	8.83	8.83 8.83
3	10.27	10.27 10.28
4	21.21	21.23 21.23

method[11] are compared with those obtained by the compleximetric titration with the Cu–EDTA–TAR system. The results obtained by both methods agree satisfactorily.

EXPERIMENTAL

Reagents

10^{-2} M EDTA standard solution. EDTA disodium dihydrate was used and the solution was standardized against a standard 10^{-2} *M* zinc solution with eriochrome black T as indicator.

$3 \cdot 10^{-2}$ M gallium solution. 2.12 g of metallic gallium (G.R.) were dissolved in a small excess of concentrated perchloric acid on a steam bath. The solution was diluted to 1 l.

$5 \cdot 10^{-3}$ M Cu–EDTA solution. An aqueous 10^{-2} *M* EDTA solution was mixed with the same volume of a 10^{-2} *M* copper(II) perchlorate solution.

TAR solution. 22.1 mg of 4-(2-thiazolylazo)resorcinol (purity 99%) was dissolved in 100 ml of dioxan.

Buffer pH 3.0–5.0. 2 *M* acetic acid solution was mixed with 2 *M* sodium acetate solution.

Apparatus

Radiometer pH Meter Model PHM 22 (Copenhagen NV. Denmark).
Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer.

Recommended procedure

To a weakly acidic sample solution containing 1–20 mg of gallium add 30 ml of a $5 \cdot 10^{-3}$ *M* Cu–EDTA solution. Adjust the pH of the solution to 3.5–4.0 with acetate buffer solution. After addition of 0.5 ml of TAR solution, titrate with a 10^{-2} *M* EDTA standard solution. Near the end-point, heat the solution to 50–70° and continue the titration dropwise. A distinct color change from lilac to light green is observed at the end-point. Titrate to a light green with no dark shade.

Appendix

The values of the formation constants used for calculation in the present paper were:

$\log K_{\mathrm{GaY}} = 20.3$, $\log K^{\mathrm{H}}_{\mathrm{GaHY}} = 1.7$[12].

$\log K_{\mathrm{CuY}} = 18.80$, $\log K^{\mathrm{H}}_{\mathrm{CuHY}} = 3.0$[12].

$\log K_{\mathrm{CuA}} = 13.66$[13], $\log K^{\mathrm{HA}}_{\mathrm{CuHA}} = 8.34$[13].

$\mathrm{p}K_{\mathrm{H_3A}} = 0.98$, $\mathrm{p}K_{\mathrm{H_2A}} = 6.17$, $\mathrm{p}K_{\mathrm{HA}} = 9.49$[13].

SUMMARY

A copper–EDTA–TAR system is proposed for the compleximetric titration of gallium. The recommended procedure for the titration was established from theoretical considerations on the equilibria involved. The color change is from lilac to light green in an acetate-buffered solution at pH 3.5–4. The method is simple and accurate for the titration of solutions containing 1–20 mg Ga per 100 ml.

RÉSUMÉ

Un système cuivre–EDTA–TAR est proposé pour le titrage compleximétrique du gallium. La méthode recommendée pour ce titrage est établie d'après les considérations théoriques sur les équilibres observés. Le changement de coloration va du lilas au vert clair, en solutions tampon acétate, au pH 3.5–4.0. Ce procédé est simple et précis pour le titrage de solutions contenant 1 à 20 mg Ga par 100 ml.

ZUSAMMENFASSUNG

Es wird ein Kupfer–EDTA–TAR-System für die komplexometrische Titration von Gallium vorgeschlagen. Das empfohlene Verfahren wurde nach theoretischer Behandlung der vorliegenden Gleichgewichte ausgearbeitet. Der Farbumschlage erfolgt von lila nach hellgrün in einer acetatgepufferten Lösung bei pH 3.5–4. Die Methode ist einfach und genau für die Titration von Lösungen mit 1–20 mg Ga pro 100 ml.

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POTENTIOMETRIC STUDIES WITH A LIQUID ION-EXCHANGE LEAD-SELECTIVE ELECTRODE

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A study was undertaken to evaluate the response and selectivity characteristics of the Orion liquid ion-exchange lead electrode with the view to its possible application for the measurement of lead activity in biological fluids. Its use as a potentiometric indicating electrode was also studied. ROSS AND FRANT[1] have reported on the use of this electrode for the potentiometric titration of sulfate with lead.

EXPERIMENTAL

Reagent grade chemicals were used throughout and solutions were prepared with distilled and deionized water. Potential measurements with the Orion liquid ion-exchange lead-specific ion electrode, No. 92-82, were made with a Keithley 610 B electrometer and the assembly previously described[2]. A saturated ammonium nitrate–3% agar bridge was used to make contact with the S.C.E. reference electrode. Potential–time curves for determining the dynamic response of the electrode were recorded on a Texas Instruments Servoriter recorder. Activities were calculated by the method of KIELLAND[3].

RESULTS AND DISCUSSION

Response characteristics

A plot of potential *vs.* logarithm of the lead activity for a freshly assembled electrode yielded a straight line with a slope of 27 mV per ten-fold change in lead ion activity over the concentration range 10^{-4}–10^{-2} M. The readings were reproducible to ±0.5 mV on the same day. After one month of use, the slope was 26.5 mV and the E^0 value had decreased slightly as indicated in Table I. The electrode functioned adequately in the concentration range $2 \cdot 10^{-5}$–10^{-2} M but optimal results were ensured at concentrations of 10^{-4} M and greater.

TABLE I

E^0 VALUES AS A FUNCTION OF CONCENTRATION AND TIME

Concentration of lead, M	*Freshly assembled*	*One month old*
10^{-5}	0.244	0.232
10^{-4}	0.231	0.221
10^{-3}	0.231	0.223
10^{-2}	0.230	0.221

The response characteristics of the electrode were evaluated by exposing the electrode to rapid changes in lead concentration and recording the resultant change in e.m.f. as a function of time. The electrode was subjected to concentration changes from dilute to concentrated lead solutions and *vice versa*. All curves were smooth and essentially constant potential readings were obtained after 2 min, although fairly reproducible readings could be recorded after 0.5 min. The electrode potential tended to drift if measurements of lead activity were made following measurements of silver, copper(II), or mineral acid solutions.

The functioning of the electrode was tested at different pH values. Solutions of lead nitrate at 10^{-2}, 10^{-3}, and 10^{-4} M were measured and the pH was adjusted by addition of nitric acid or sodium hydroxide. Results are summarized in Fig. 1. The optimum pH ranges for the electrode for solutions of 10^{-2} M, 10^{-3} M, and 10^{-4} M lead were 3.5–6.0, 4.6–6.5 and 5.0–6.8, respectively. In view of variations of the electrode response to monovalent cations from one electrode to another (see below), it is likely that these pH ranges will differ somewhat for different electrodes.

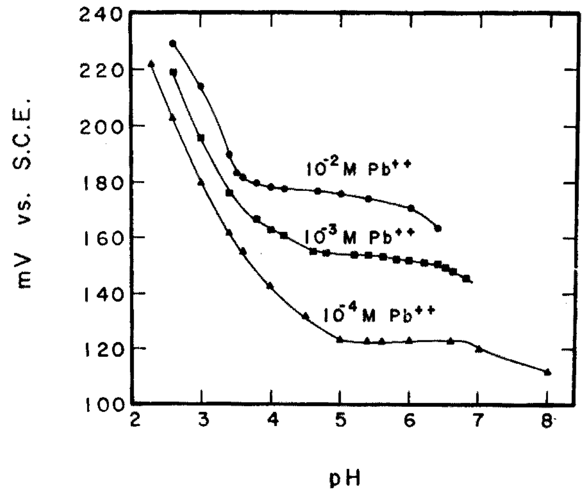


Fig. 1. Electrode response as a function of pH.

Selectivity ratios

The response of the electrode to different ions relative to lead ion was determined by calculating selectivity ratios, through the modified Eisenman equation[4]. The equation used to define the potential for a mixture of lead with a monovalent ion is

$$E = E^0_{Pb} + \alpha \log\,(a_{Pb^{2+}} + K_{PbM}[a_{M^+}]^2)$$

and that for a mixture with a divalent ion is

$$E = E^0_{Pb} + \alpha \log\,(a_{Pb^{2+}} + K_{PbM}a_{M^{2+}})$$

where E^0_{Pb} is a constant and can be determined from the potential with a pure lead solution (see Table I) and α is the experimental slope of potential *vs.* activity, 27 mV; K_{PbM} is the selectivity ratio for the ion, M, over lead. Table II summarizes the selectivity ratios calculated for different ions at different concentrations.

TABLE II

SELECTIVITY RATIOS FOR DIFFERENT IONS AT DIFFERENT CONCENTRATIONS

Ion	*Selectivity ratio at*				
	10^{-5} *M*	10^{-4} *M*	10^{-3} *M*	10^{-2} *M*	10^{-1} *M*
H^+	1.9×10^{7}	4.2×10^{5}	2.9×10^{5}	1.0×10^{3}	1.1
Ag^+	2.2×10^{6}	1.7×10^{5}	8.6×10^{4}	5.6×10^{2}	9.0×10^{-1}
Na^+	8.9×10^{6}	5.6×10^{4}	2.6×10^{2}	2.0	3.0×10^{-2}
K^+	8.9×10^{6}	3.5×10^{4}	3.0×10^{2}	3.0	8.6×10^{-3}
Cu^{2+}	1.2×10^{3}	1.8×10^{2}	1.4×10^{2}	2.6	2.2×10^{-1}
Ca^{2+}	2.5×10^{1}	2.6	3.4×10^{-1}	3.5×10^{-2}	5.0×10^{-3}
Mg^{2+}	1.7×10^{3}	1.7×10^{2}	1.7×10^{1}	6.9×10^{-1}	9.2×10^{-2}
Ni^{2+}	8.9	1.3	2.8×10^{-1}	1.1×10^{-2}	2.9×10^{-3}
Zn^{2+}	1.0×10^{1}	3.0	2.4×10^{-1}	3.0×10^{-2}	2.3×10^{-3}

It is apparent that the calculated selectivity ratios for the interfering ions change with changing concentration of the ion. In all cases, the relative selectivity toward lead increases with increasing concentration of interfering ion. This is due to a decrease in the E^0 values used for the calculation of selectivity ratios of the interfering ion, and is similar to behavior reported for a potassium ion-selective electrode[2]. The calculated selectivity ratios indicate that the electrode is much more responsive to monovalent cations than reported by the manufacturer. The values for selectivities reported here are only relative and depend on factors such as the age of the electrode.

TABLE III

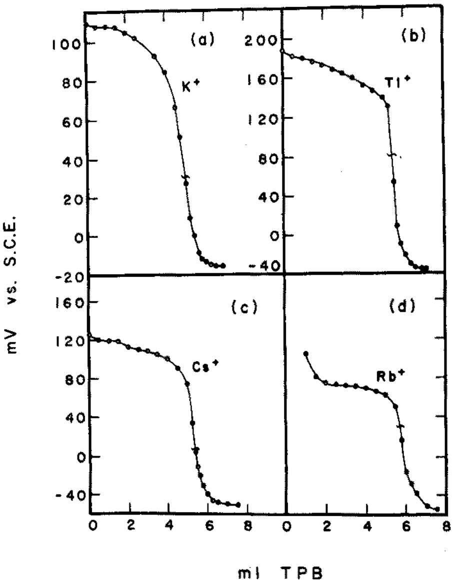
SELECTIVITY RATIOS DETERMINED FOR TWO DIFFERENT ELECTRODES

Ion	*Selectivity ratio*			
	Electrode I		*Electrode II*	
	10^{-3} *M*	10^{-2} *M*	10^{-3} *M*	10^{-2} *M*
Na^+	100	0.85	126	0.96
K^+	137	1.3	108	0.93
Rb^+	440	1.6	12	0.18
Cs^+	476	1.9	21	0.33
NH_4^+	440	1 9	50	0.33
Tl^+	761	10	7.6	0.42
Ag^+	6.3×10^{5}	3.6×10^{3}	9.2×10^{5}	2.6×10^{5}
H^+	6.3×10^{5}	276	9.6×10^{6}	1.5×10^{3}
Ca^{2+}	1.6	0.11	0.035	0.016
Mg^{2+}		0.07	0.29	0.04
Ni^{2+}	0.50	0.055	0.19	0.06
Mn^{2+}	0.18	0.09	0.11	0.013
Fe^{2+}	0.36	0.096	0.34	0.052
Zn^{2+}	0.14	0.14	0.63	0.08
Cu^{2+}	5.2	1.0	3.5	0.85

The high response toward monovalent ions was confirmed with two different electrodes and different filling solutions. Results for the two electrodes are summarized in Table III. Although the absolute values of selectivity ratios varied somewhat from one electrode to the other, as did the relative ratios at different concentrations, it is apparent from these data that both electrodes exhibited selectivities to monovalent ions at 10^{-3} *M* of greater than unity and near unity at 10^{-2} *M*.

Titration of monovalent cations

The results for the monovalent cations suggest that the electrode should be useful for potentiometric titrations of these ions. Titrations of potassium, rubidium, cesium, thallium(I), silver(I), and ammonium ions with sodium tetraphenylboron were attempted and typical titration curves are illustrated in Figs. 2 and 3. Solutions were buffered with acetic acid–sodium acetate buffer. The equivalence points are marked on the curves and indicate that the titrations can be performed with good accuracy. These results confirm the electrode response to monovalent cations determined from the selectivity measurements. The electrode possesses advantage over a potassium glass electrode for the potentiometric titration of potassium ion with sodium tetraphenylboron. With the glass electrode, the calcium salt of tetraphenylboron must be used to obtain sharp end-points[5]. With the present electrode the sodium salt can be used, even though the electrode exhibits essentially equal response to sodium ion. This might be due to a response to the tetraphenylborate ion.



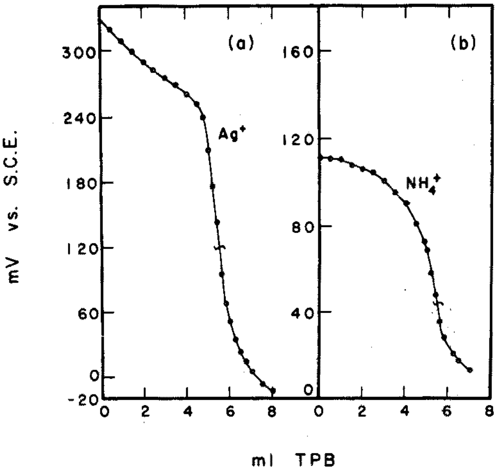


Fig. 2. Potentiometric titrations with sodium tetraphenylboron:
(a) 50 ml 10^{-3} *M* KCl, pH 3;
(b) 50 ml 10^{-3} *M* $TlNO_3$, pH 3;
(c) 50 ml 10^{-3} *M* CsCl, pH 3;
(d) 50 ml 10^{-3} *M* RbCl, pH 3.

Fig. 3. Potentiometric titrations with sodium tetraphenylboron:
(a) 50 ml 10^{-3} *M* $AgNO_3$, pH 3;
(b) 50 ml 10^{-3} *M* NH_4Cl, pH 3.

Titration of lead(II)

The usefulness of the electrode for the potentiometric titration of lead with various precipitating agents was tested. Typical S-shaped titration curves with sharp end-point breaks were obtained for the titration of 100 mg of lead in a volume of 50 ml, with 0.01 *M* solutions of sodium oxalate, potassium sulfate, potassium chromate, potassium hexacyanoferrate(III), potassium pyrophosphate, and sodium tungstate. Table IV summarizes the results of the titrations. The electrode did not respond well in the presence of iodide and iodate ions and no reliable potentiometric titration curves for these reagents could be obtained. Similarly, the electrode failed to respond in the presence of most organic reagents and titrations of lead with salicylaldoxime, EDTA, and dithizone were unsuccessful.

TABLE IV

POTENTIOMETRIC TITRATIONS OF LEAD WITH DIFFERENT PRECIPITATING AGENTS

(103.6 mg of lead was taken in each case)

Reagent	*Lead found (mg)*	*Error (%)*
$Na_2C_2O_4$	104.2	+0.6
K_2SO_4	103.4	−0.2
K_2CrO_4	105.6	+1.9
$K_4Fe(CN)_6$	106.7	+2.9
$K_4P_2O_7$	100.1	−3.3
Na_2WO_4	105.6	+1.9

SUMMARY

The performance of the Orion liquid ion-exchange lead-selective electrode has been determined in terms of the working concentration range of lead ions, its selectivity to other ions, its response time, the effective pH range in which it can be used, and its use in potentiometric titrations. The electrode exhibits relatively high response to monovalent cations and can be used in the potentiometric titration of alkali metals, thallium(I), silver(I), and ammonium ions with sodium tetraphenylboron, as well as for titrations of lead(II) with various solutions.

RÉSUMÉ

Une étude est effectuée sur les possibilités de l'électrode sélective Orion de plomb: limites de concentration, sélectivé vis à vis d'autres ions, temps de réponse, limites de pH et son utilisation pour des titrages potentiométriques. L'électrode présente une relativement haute réponse pour les cations monovalents; elle peut être utilisée pour le dosage potentiométrique des métaux alcalins, du thallium(I), de l'argent(I) et des ions ammonium, à l'aide de sodium tétraphénylbore, de même que pour des titrages de plomb dans diverses solutions.

ZUSAMMENFASSUNG

Die Leistungfähigkeit der bleiselektiven, auf flüssigem Ionenaustausch beruhenden Orion-Elektrode ist untersucht worden bezüglich der Bleiionen-Arbeitskonzentration, der Selektivität gegenüber anderen Ionen, der Ansprechzeit, des pH-Bereiches und der Anwendung bei potentiometrischen Titrationen. Die Elektrode spricht relativ stark auf einwertige Kationen an und kann für die potentiometrische

Titration von Alkalimetall-, Thallium(I)-, Silber(I)- und Ammoniumionen mit Natriumtetraphenyloborat ebenso wie für Titrationen mit Blei(II) mit verschiedenen Lösungen benutzt werden.

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APPLICATION OF SILICONE RUBBER-BASED GRAPHITE ELECTRODES FOR CONTINUOUS FLOW MEASUREMENTS

PART II. VOLTAMMETRIC STUDY OF ACTIVE SUBSTANCES INJECTED INTO ELECTROLYTE STREAMS

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(Received April 20th, 1970)

Previous studies[1,2] have shown that silicone rubber-based graphite electrodes are suitable for the determination of many inorganic and organic compounds by means of their reduction or oxidation in the potential range of −0.5 to +1.5 V (*vs.* S.C.E.) in static electrolyte solutions. The applicability of these graphite electrodes for analysis in flowing media has also been demonstrated[3]. A linear relationship was found between the current intensity measured at constant potential and the concentration of the streaming solution, while the current intensity showed a linear dependence on the square root of the flow rate in the range investigated. Thus, the detector cell was suitable for the determination of the concentration of an electroactive species in a solution having a constant flow rate, or it was possible to measure the rate of flow of a solution of constant concentration. The accuracy of both measurements was found to be satisfactory. This method rendered possible continuous process control of industrial equipment.

In the present paper, the development of an appropriate measuring technique for rapid serial analyses of samples of small volume by means of the detector cell reported previously[3], is described. The voltammetrically active compound was injected into a flow of supporting electrolyte and the signals of the detector cell were studied as a function of the concentration and the rate of flow. As the response of the detector cell was experimentally proved to be practically instantaneous, it was possible to detect easily the concentration or the rate of flow in the cell.

EXPERIMENTAL

Equipment

The response time of the electrode was measured by means of a Polymetron Polyrecorder type 120 equipped with an adapter to record current intensity. The recorder was connected in series to the measuring cell and a Radelkis Polarograph type OH 101/1. In order to measure the response time of the Polyrecorder, a resistance was inserted in the circuit instead of the cell.

The experimental set-up is shown in Fig. 1. The indicator electrode was a

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microelectrode having a surface area of 0.25–2 mm^2. The silicone rubber layer filled with graphite was fixed to the end of a capillary tube containing a drop of mercury to secure the electric contact. A silver–silver chloride electrode, immersed in the flowing 0.1 *M* potassium chloride solution was used as reference electrode.

A hydrostatic method was employed to ensure the constant flow of the supporting electrolyte. Constant pressure was provided by a level controller. The flow rate was determined by measuring the volume of the solution leaving the system in the unit of time.

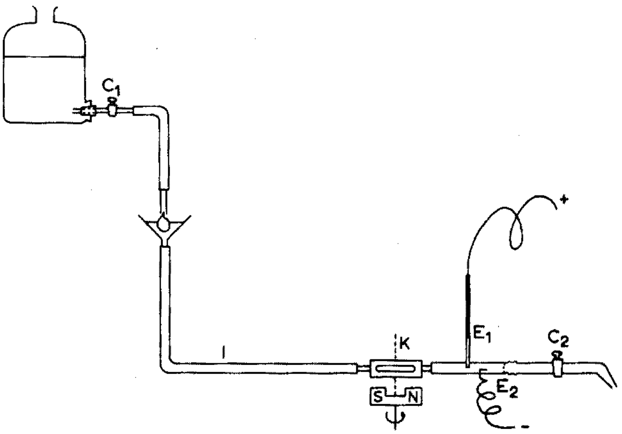


Fig. 1. Experimental set-up. (K) Stirrer; (C_1 and C_2) stopcocks; (E_1) indicating microelectrode; (E_2) reference electrode. The reservoir contains 0.1 *M* potassium chloride.

The injection of the voltammetrically active solution into the stream of the supporting electrolyte was performed by means of a Hamilton type syringe through a rubber tube inserted into the system. A magnetic stirrer placed between the tube serving for the injection and the measuring cell ensured the reproducibility of the measurement.

Materials

The supporting electrolyte was prepared from reagent-grade potassium chloride. Propylon {3,4-dihydroxy-α-(isopropylaminomethyl)-benzyl alcohol} hydrochloride was employed as the model substance.

RESULTS

The response time of the electrode

The response time of the electrode was defined by the time interval between the instant when the electrode came in contact with the solution and that, when the signal attained its maximum value. The response time was calculated from the difference in the response time of the Polyrecorder signal obtained when a suitable resistance and the cell respectively were inserted in the circuit (Fig. 2). It is apparent from Fig. 2, that the response time was practically equal in both cases, *i.e.* the response time of the electrode to concentration changes is less than 1 s.

Relation between the amount of the injected electroactive substance and the voltammetric signal

Various amounts of an electroactive material were injected in equal volumes into the supporting electrolyte stream at a constant flow rate. The potential of the electrode was set to an appropriate constant value. The area under the peak was proportional to the amount of material injected at identical rates of flow as shown in Fig. 3; the area under the peak was determined by weighing the cut-out plot.

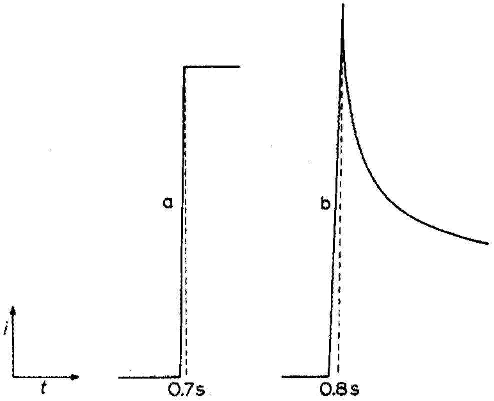


Fig. 2. A comparison between the response time of the instrument (a) and the indicator electrode (b).

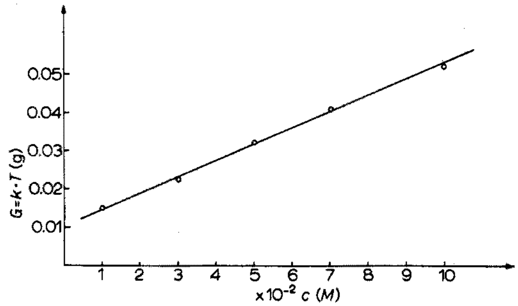


Fig. 3. Relation between the concentration of solution injected and the area under the peak. Potential, + 1.0 V; sensitivity, $1\cdot10^{-8}$ A mm^{-1} and $4\cdot10^{-9}$ A mm^{-1}; flow rate, 0.106 ml s^{-1}; sample injected, 0.1 ml.

Reproducible results were obtained only if a rapid and total homogenization of the solution to be analyzed and the supporting electrolyte was ensured. Preliminary experiments and visual observation of the stream lines by a suitable technique showed that the test solution injected into the supporting electrolyte flowing in a straight tube did not mix with the latter to the desired extent even at high flow rates. The reproducibility of the measurements was impeded by a concentration gradient perpendicular to the direction of flow. This concentration gradient was influenced by many factors. However, reproducible results were obtained when a magnetic stirrer was employed, and this was found to provide the best solution of the problem in hand.

Effect of the rate of injection

The influence of the rate of injection on the measured signal was also investigated. A comparatively large amount, *i.e.* 1 ml of $3 \cdot 10^{-2}$ M Propylon solution was injected into the supporting electrolyte flowing at a constant rate, while the time of injection was varied. The area under the peak as a function of the rate of injection is shown in Fig. 4.

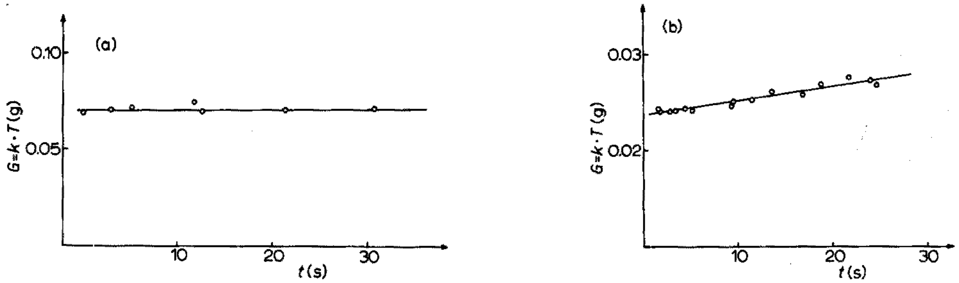
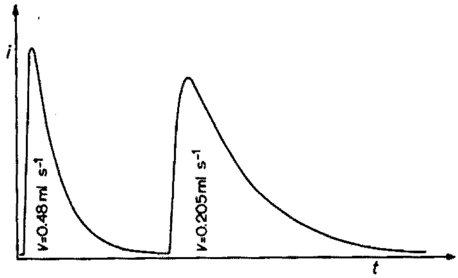


Fig. 4. Effect of the rate of injection on the area under the peak. Potential, + 1.0 V; sensitivity, $2 \cdot 10^{-8}$ A mm^{-1}; flow rate, (a) 0.110 ml s^{-1}, (b) 0.392 ml s^{-1}.

Relation between the rate of flow and the voltammetric signal

The signals shown in Fig. 5 were obtained by injection of equal volumes (0.1 ml) of $5 \cdot 10^{-2}$ M solution into a supporting electrolyte streaming at various flow rates. The area under the peak as a function of the flow rate is represented in Fig. 6.



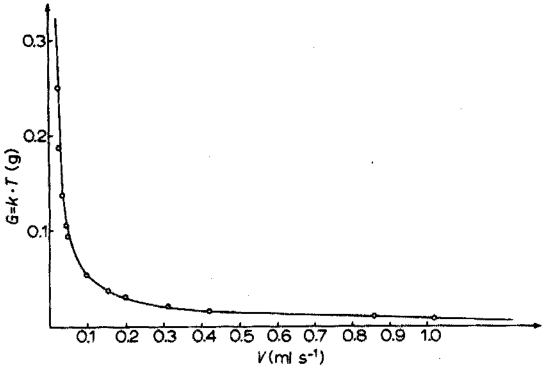


Fig. 5. Signals obtained for injection into the supporting electrolyte at two different flow rates. Propylon concentration, $1 \cdot 10^{-2}$ M; sensitivity, $3 \cdot 10^{-9}$ A mm^{-1}; sample injected, 0.1 ml.

Fig. 6. Dependence of the area under the peak on the flow rate of the supporting electrolyte. Potential, + 1.0 V; sensitivity, $4 \cdot 10^{-9}$ A mm^{-1} and $8 \cdot 10^{-9}$ A mm^{-1}; Propylon concentration $5 \cdot 10^{-2}$ M; sample injected, 0.1 ml.

INTERPRETATION OF RESULTS

The area under the peak was practically unaffected by the rate of injection over a large range (1–30 s). At very high flow rates the height of the peak was found to increase. In order to avoid this effect a small volume of solution (0.1 ml) was injected at high rate to ensure a "plug"-form injection.

On the basis of the linear relation found between the area under the peak and the concentration of the solution, the latter can be determined by this method. It can advantageously be employed in serial analysis as it is not necessary to dilute concentrated solutions or to mix them with the supporting electrolyte, and further, a small amount of sample is sufficient for the determination. The method is very rapid, especially if the area under the peak is measured by means of an integrator.

The flow rate of solutions can also be measured by this technique, as the signal produced by a small volume of a solution of a known concentration injected just before the cell, is proportional to the flow rate of the supporting electrolyte.

The variation of the concentration as a result of the amount of material injected in the cell

The theoretical studies were based on the following assumptions, which represent a fairly good approximation of the real measuring conditions:

1. The rate of injection was constant, *i.e.* no concentration gradient was formed in the direction of flow in the plug of liquid containing the electroactive material.

2. The mixing of the solution in the unit used for stirring was instantaneous.

3. According to condition 2, the concentration of the solution emerging from the stirring unit was always equal to that prevailing inside the stirring unit. Thus it was sufficient to study the relation inside this unit.

The concentration inside the stirring unit increased after the injection of the sample, attained its maximum value and then decreased to zero. Thus, the problem could be divided into two parts: increase and decrease of the concentration.

As the injected sample enters the stirring unit in a portion of the streaming supporting electrolyte, the average concentration ($\bar{c}$) of a solution segment perpendicular to the direction of flow is given by

$$\bar{c} = \frac{M}{V\tau} \tag{1}$$

where M is the amount of sample injected into the system, V is the flow rate, and τ is the time required by the portion of liquid containing the injected material to traverse the cross-section of the tube preceding the stirring unit. If "tailing" is ignored, this is equal to the time of injection.

If c is the concentration inside the stirring unit of volume W, the difference in the concentrations at the inlet and the outlet of the stirring unit, *i.e.* the concentration variation during the time interval, dt, is given by

$$\mathrm{d}c = \frac{1}{W}\left(\frac{M}{V\tau}\cdot V\mathrm{d}t\right) - \frac{c\,V\mathrm{d}t}{W} \tag{2}$$

i.e.

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{M}{W\tau} - \frac{V}{W}c \tag{3}$$

The general solution of the differential equation is:

$$c = [(M/W\tau) - \mathrm{const}\cdot\exp-(V/W)t](W/V) \tag{4}$$

Assuming the initial conditions $t=0$ and $c=0$, then the constant is equal to $M(\tau W)^{-1}$, thus:

$$c=(M/V\tau)[1-\exp-(V/W)t] \tag{5}$$

When the liquid containing the sample has passed through the inlet of the stirring unit, the concentration in the latter begins to decrease under the effect of the supporting electrolyte according to the following equation:

$$\mathrm{d}c=-c(V/W)\mathrm{d}t \tag{6}$$

The general solution of the differential equation is:

$$c=\mathrm{const}\cdot\exp-(V/W)t \tag{7}$$

The process begins when $t=\tau$, thus the equation can be rewritten as follows:

$$c=\mathrm{const}\cdot\exp-(V/W)(t-\tau) \tag{8}$$

As $c=c_{\mathrm{max}}$ at $t=\tau$, the constant can be evaluated from the equation giving the increase in the concentration:

$$c_{\mathrm{max}}=(M/V\tau)[1-\exp-(V/W)\tau] \tag{9}$$

Accordingly, the equation for the decrease of the concentration is:

$$c=(M/V\tau)[1-\exp-(V/W)\tau]\exp\{-(V/W)(t-\tau)\} \tag{10}$$

The effect of change in concentration and in flow rate on the voltammetric signal

The voltammetric signal obtained in flowing media at constant potential is a function of the concentration and the flow rate.

According to LEVICH's theory[4], the intensity of the voltammetric current is:

$$i=knFD^{2/3}\,\nu^{-1/6}\,c\cdot V^{1/2} \tag{11}$$

where k is constant, n is the number of electrons taking part in the electrode reaction, F is the Faraday number, D is the diffusion coefficient, ν is the kinematic viscosity, c is the concentration of the electroactive component, V is the flow rate.

According to the present results, in some cases the diagram of the voltammetric current *vs.* the square root of the flow rate extrapolated to zero flow rate intersected the ordinate at a positive value of the current intensity, which depended on the concentration of the electroactive component.

In such cases, eqn. (11) must be modified as follows:

$$i=knFD^{2/3}\,\nu^{-1/6}\,c\,(a+V^{1/2}) \tag{12}$$

where a is constant. If $knFD^{2/3}\,\nu^{-1/6}$ is denoted by K, then at time t it follows that:

$$i_t=K\cdot c_t\,(a+V^{1/2}) \tag{13}$$

Introducing the correlations concerning the concentration then:
if $t\leqq\tau$

$$i_t=K(a+V^{1/2})(M/V\tau)[1-\exp-(V/W)t] \tag{14}$$

if $t\geqq\tau$

$$i_t=K(a+V^{1/2})(M/V\tau)[1-\exp-(V/W)\tau]\exp\{-(V/W)(t-\tau)\} \tag{15}$$

The area under the curve is obtained by solving the following integral equation:

$$T=(KM/V\tau)(a+V^{1/2})\left[\int_0^{\tau}\{1-\exp-(V/W)t\}\mathrm{d}t+\{1-\exp-(V/W)\tau\}\int_{\tau}^{\infty}\{\exp-(V/W)(t-\tau)\}\mathrm{d}t\right]$$

The solution of the above equation is:

$$T=KM/V(a+V^{1/2}) \tag{16}$$

Comparison of the calculated results with the experimental results

Equation (16) predicts a linear relation between the amount of the injected substance and the area under the surface. This is in good agreement with the calibration curve shown in Fig. 3.

To facilitate the comparison of the experimental results with the formula giving the relation between the flow rate and the area under the curve, eqn. (16) can be rewritten in the following form if M = const, *i.e.* when equal amounts of substances are injected:

$$T=(A/V)+(B/V^{1/2}) \tag{17}$$

where A and B are constants, V is the flow rate, and T is the area under the peak.

The constants A and B can be calculated from the area under the curve obtained at two different rates of flow; 0.1 ml of a $5\cdot10^{-2}$ M solution was injected in the supporting electrolyte streaming at rates of 0.1 and 0.2 ml s^{-1}, and the areas under the curves were calculated in each case. The following values were obtained for the constants: $A=0.00408$ and $B=0.00381$.

The curve obtained by introducing these values into eqn. (17), and the measured values show good agreement as can be seen in Fig. 7.

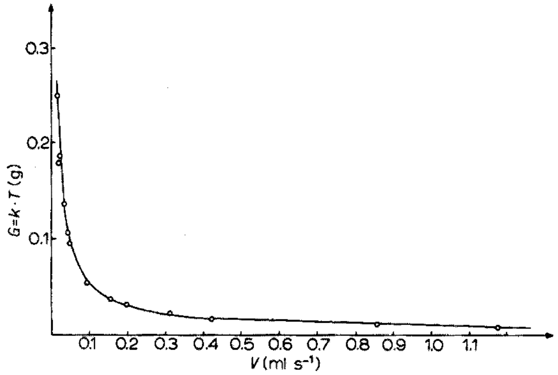


Fig. 7. Comparison between the results calculated and obtained experimentally. (—) Theoretical curve; (o) values measured.

SUMMARY

A technique has been developed for the rapid analysis of samples injected into a streaming supporting electrolyte in small volumes. At constant potential the peak area of the voltammetric signal is proportional to the amount of electroactive material injected. The parameters of the determination were studied and interpreted theoretically. The experimental results are in good agreement with theory.

RÉSUMÉ

Une technique est proposée pour l'analyse rapide d'échantillons injectés dans un courant d'électrolyte de base, en faible volume. A potentiel constant, la surface du pic du signal voltammétrique est proportionnelle à la teneur de la substance électroactive injectée. Les paramètres du dosage sont étudiés et interprétés théoriquement. Les résultats expérimentaux correspondent bien à la théorie.

ZUSAMMENFASSUNG

Es ist ein Verfahren für die schnelle Analyse von Proben entwickelt worden, die in kleinen Volumina in einen strömenden Trägerelektrolyten injiziert werden. Bei konstantem Potential ist die Peak-Fläche des voltammetrischen Signals der Menge des injizierten elektroaktiven Stoffes proportional. Die Parameter der Bestimmung wurden untersucht und theoretisch gedeutet. Die experimentellen Ergebnisse stimmen mit der Theorie gut überein.

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REACTIONS ACIDE–BASE DANS L'ACIDE TRIFLUOROACETIQUE ET DANS QUELQUES MILIEUX ACIDES

COMPARAISON DE LA FORCE RELATIVE DES ACIDES ET DES BASES

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L'échelle acide–base étant déterminée dans l'acide trifluoroacétique[1], il est intéressant de comparer les réactions acido–basiques dans ce solvant avec celles étudiées dans certains milieux acides tels l'acide acétique ou les mélanges eau–acide sulfurique, et de voir ainsi dans quelle mesure les règles simples de prévision des réactions en solution dans un solvant donné à partir d'un milieu de référence[2,3] sont applicables au cas de l'acide trifluoroacétique.

L'utilisation de la fonction H_0 de HAMMET[4] généralisée au cas des milieux peu dissociants[5,6] permet de comparer les acidités et basicités relatives des solvants acides–carboxyliques suivants: acide formique, acide acétique, acide dichloroacétique et acide trifluoroacétique.

Par ailleurs, elle rend possible l'étude des variations de l'étendue du domaine d'acidité des solvants constitués par les mélanges acide trifluoroacétique–eau et acide trifluoroacétique–acide acétique.

PARTIE THÉORIQUE

Comparaison entre un solvant dissociant, l'eau et un solvant HS peu dissociant

L'examen d'un même équilibre chimique dans plusieurs solvants permet de définir un certain nombre de corrélations à partir desquelles il est possible de prévoir cet équilibre dans un milieu quelconque. Il est commode de choisir comme solvant de référence l'eau, solvant dans lequel un grand nombre de réactions sont connues.

La comparaison des équilibres chimiques entre l'eau et l'acide trifluoroacétique se heurte à une difficulté du fait que le premier milieu est dissociant ($\varepsilon = 78.6$), alors que le second l'est peu ($\varepsilon = 8.4$)[7]. Les échelles acide–base sont donc de nature différente. Dans le premier cas, la prévision des réactions s'effectue à partir d'une échelle de pH qui est une échelle ionique; dans le second cas, c'est une échelle moléculaire qui rend compte des phénomènes[8].

On ne peut en fait, comparer ces échelles que dans la mesure où les réactions acide–base envisagées font intervenir deux couples de même type. Ainsi, si l'on considère le comportement de deux bases non chargées B_1 et B_2 vis-à-vis d'un même acide fort HX dans chacun des deux solvants, les équilibres sont les suivants:

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \text{ (eau) avec } K_{H_2O} = \frac{[B_2H^+][B_1]}{[B_1H^+][B_2]}$$

$$B_1HA + B_2 \rightleftharpoons B_2HA + B_1 \text{ (solvant peu dissociant) avec } K_{HS} = \frac{[B_2HA][B_1]}{[B_1HA][B_2]}$$

La constante K_{H_2O} exprime la différence de basicité de B_1 et B_2 dans l'eau. La constante K_{HS} peut être considérée comme le produit de deux constantes, la première caractérisant la différence d'affinité de B_1 et B_2 pour le proton solvaté H^+ dans le solvant HS, la seconde caractérisant la différence d'affinité des ions B_1H^+, et B_2H^+ pour l'anion A^- dans ce même milieu. La première constante traduit donc la différence de basicité vraie entre B_1 et B_2 dans le solvant HS et la constante K_{HS} ne représente qu'une différence de basicité apparente de B_1 et B_2 dans le solvant HS; elle dépend de la nature de l'anion de l'acide fort.

L'échelle moléculaire unique ne rend compte de la différence de basicité vraie entre les deux brases B_1 et B_2 que dans la mesure où les paires d'ions mises en jeu au cours de la réaction, ont le même pK de dissociation ionique. C'est généralement l'hypothèse admise dans le cas des solvants protoniques peu dissociants. Elle a été partiellement vérifiée dans le cas de l'acide trifluoroacétique[9]. Dans ces conditions, les forces relatives des bases B_1 et B_2 sont conservées dans l'eau et le solvant HS si $K_{H_2O} = K_{HS}$.

Les réactions mettant en jeu une base B non chargée et un acide HA non chargé sont de nature différente en milieu dissociant et en milieu peu dissociant. Elles mettent en jeu les couples $BH^+|B$ et $HA|A^-$, qui ne sont pas de même type[2]. Dans le premier cas, la réaction est à quatre termes: $B + HA \rightleftharpoons BH^+ + A^-$; dans le second, elle est à trois termes: $B + HA \rightleftharpoons BHA$. Ces constantes d'équilibre n'étant plus "homogènes", il n'est plus possible de les comparer comme dans le cas précédent.

Coefficients de solvatation—Règles de prévision des réactions

Si l'on considère à nouveau la réaction traduisant la différence de basicité de B_1 et B_2 dans l'eau et le solvant peu dissociant HS, il est possible de relier simplement les constantes K_{H_2O} et K_{HS} en introduisant la notion de coefficient de solvatation[10,11].

Si l'on représente pat Γ_B et Γ_{BH^+} les coefficients de solvatation de la molécule B et du cation solvaté BH^+, ces coefficients traduisant la différence de solvatation de ces deux espèces entre le solvant HS et l'eau, on a la relation:

$$K_{H_2O} = K_{HS} \cdot \frac{\Gamma_{B_1}}{\Gamma_{B_1H^+}} \cdot \frac{\Gamma_{B_2H^+}}{\Gamma_{B_2}}$$

On suppose que les paires d'ions n'ont pas d'influence et que K_{HS} mesure la différence de basicité vraie entre B_1 et B_2.

La prévision des réactions acide–base dans un milieu donné à partir d'un solvant de référence s'effectue à partir de quelques hypothèses simplificatrices, qui se trouvent assez bien vérifiées expérimentalement.

L'une d'entre elles consiste à admettre que le pK d'une réaction mettant en jeu deux couples acide–base de même nature, ne varie pas d'un milieu à l'autre. La relation précédente montre que cette hypothèse implique que tous les couples $BH^+|B$ soient caractérisés par une même valeur du rapport Γ_B/Γ_{BH^+}, autrement dit, elle suppose que la différence de solvatation entre B et BH^+ reste constante lorsque l'on passe de l'eau, solvant de référence, au milieu étudié. Il en est de même pour tous les couples HA|A$^-$ pour lesquels le rapport Γ_{AH}/Γ_{A^-} a une valeur identique, différente de celle relative aux couples BH$^+$|B.

Une seconde hypothèse simplificatrice[2,4,12] consiste à admettre que pour tous les couples BH$^+$|B, $\Gamma_{BH^+} = \Gamma_B$. Cela revient à supposer que la solvatation de la base B et du cation BH$^+$ est la même d'un solvant à l'autre.

C'est dans le but d'appliquer ces raisonnements simples que sont définies par rapport à l'eau deux échelles générales pK_{H_2O}, l'une relative aux couples BH$^+$|B, l'autre aux couples HA|A$^-$ à partir desquelles il est possible de prévoir les réactions acide–base dans un solvant donné[2].

Il est important de souligner que ces hypothèses ne sont valables qu'en première approximation et qu'elles peuvent se trouver en défaut dans le cas de certains solvants ou de certains couples acide–base; il n'en reste pas moins vrai qu'elles sont relativement satisfaisantes et fort utiles dans de nombreux cas, surtout lorsqu'il s'agit des couples HB$^+$|B.

La détermination expérimentale de la force des acides HA non chargés et des bases B non chargées dans plusieurs solvants acides, permet d'apprécier la validité de ces hypothèses et de préciser ses limites d'application, notamment dans le cas de l'acide trifluoroacétique.

CLASSEMENT DES BASES

L'acide trifluoroacétique ayant des propriétés basiques faibles, les solvants de comparaison ne peuvent être que des milieux dont le caractère basique est voisin ou moins marqué que celui de CF_3COOH. Les données de la littérature relatives aux bases étudiées se rapportent essentiellement aux mélanges eau–acide sulfurique et à l'acide acétique. Quelques valeurs de pK déterminées dans d'autres solvants sont citées dans le tableau I. On se borne à comparer les résultats obtenus dans CF_3COOH avec ceux acquis dans les solvants H_2O, H_2SO_4 et CH_3COOH.

La position de chaque base B dans chacun des milieux considérés est caractérisée par rapport à celle d'un indicateur de HAMMETT, la dichloro-2,4-nitro-6-aniline dont le pK rapporté[12] à l'eau est égal à -3.30.

TABLEAU I

CONSTANTES CARACTÉRISTIQUES DES BASES DE HAMMETT DANS PLUSIEURS SOLVANTS ACIDES

Bases de Hammett	*CF_3COOH*	*Ref.*	*$H_2O + H_2SO_4$*	*Ref.*	*CH_3COOH*	*Ref.*
Anthraquinone	-8.2		-8.2	16		
Bromo-6-dinitro-2,4-aniline	-6.7	13	-6.7	16		
Chloro-4-dinitro-2,6-aniline	-6.1		-6.1	16		
Dinitro-2,6-aniline	-5.5		-5.5	16		
Dinitro-2,4-aniline	-4.5		-4.5	16		
Dichloro-2,6-nitro-4-aniline	-2.9		-3.3	16		
Dichloro-2,4-nitro-6-aniline	-3.3		-3.3	16	-3.5	2
Nitro-4-diphénylamine	-2.1	13	-2.1	12	-2.3	19
Chloro-4-nitro-2-aniline	-1.0	14	-1.0	17	-1.0	19
Benzilidène acétophénone	-4.0	15	-3.9	15		
Nitro-4-azobenzène	-3.4		-3.4	12		
Azobenzène	-2.5		-1.6	18	0.0	3
Bromo-4-azobenzène	-2.5		-2.2	18		
Méthyl-3-azobenzène	-2.5		-1.1	18		

TABLEAU II

CONSTANTES RELATIVES AUX AUTRES BASES

Bases	CF_3COOH	$H_2O + H_2SO_4$	*Ref.*	CH_3COOH	*Ref.*	*Autres solvants*	*Ref.*
Acétone	−6.7	−7.2	21	−3.3	20		
Acide acétique	−6.7	−6.1	22	−5.4			
Acétate d'éthyle	−6.5					−5.2 (acétate d'éthyle)	27
Eau	−6.9	−1.5		−2.3	20	−3.4 (acide formique)	26
Méthanol	−5.8	−2.2	23	−3.3	20		
Ethanol	−5.7	−2.3	23	−3.1	20		
Oxyde de diéthyle	−5.2	−3.6	25	−3.8	20		
Isopropanol	−5.2	−3.2	23	−2.9	20		
Acétonitrile	−4.8	−9.5	24	−4.2	20		
Propionitrile	−4.7			−4.2		−3.9 (acide formique)	26
Diméthylamino-4-azobenzène	−3.8	−1.3	2				

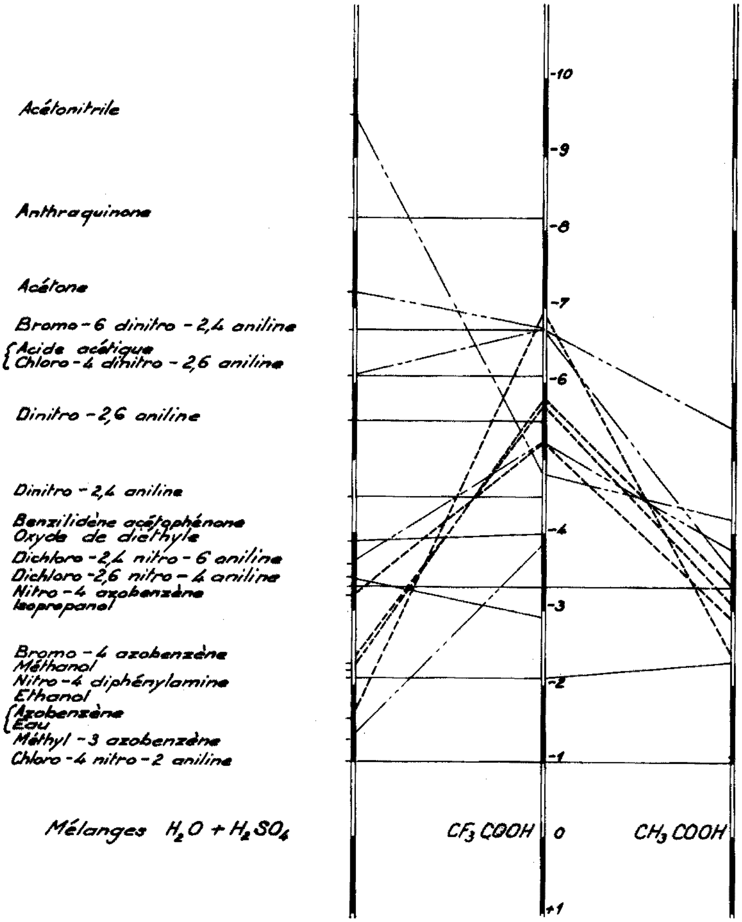

Fig. 1. Comportement des couples $HB^+|B$ dans divers milieux acides.

Dans le Tableau I figurent les constantes caractéristiques des bases de HAMMETT dans l'acide trifluoroacétique, les mélanges eau–acide sulfurique et l'acide acétique. Dans le Tableau II sont groupées les constantes relatives aux autres bases B.

Discussion

Quelle que soit l'échelle acide–base envisagée (Fig. 1) les bases de HAMMETT (excepté une interversion) conservent leurs positions respectives et ce, avec une bonne précision. Cela est lié au fait que ces indicateurs ont tous des structures très voisines, bien que de fonction chimique différente[12,26]. Dans la famille des alcools, le classement est conservé lorsque l'on passe de l'acide acétique à l'acide trifluoroacétique; il est différent dans les mélanges eau–acide sulfurique. Pour les deux composés nitrile étudiés, ces déterminations dans l'acide acétique ont montré que le propionitrile occupe une position très voisine de celle de CH_3CN, comme dans l'acide trifluoroacétique. Enfin, pour les composés azoïques, certains comme le nitro-4-azobenzène, l'azobenzène, le bromo-4-azobenzène, le méthyl-3-azobenzène se comportent comme des bases de HAMMETT, alors que d'autres, tels le diméthylamino-4-azobenzène et l'amino-4-azobenzène, voient leurs positions relatives varier différemment des précédentes.

En première approximation, il semble donc que dans une même famille chimique de composés (anilines, alcools, nitriles, et certains azoïques), la force relative des constituants de cette famille soit conservée, quel que soit le solvant.

La comparaison des positions des bases B par rapport à celle de la chloro-4-nitro-2-aniline, indicateur qui figure par convention sur une même horizontale dans les trois solvants, conduit à distinguer deux groupes de composés: le premier rassemble les bases de HAMMETT, l'acétone, l'acétonitrile, le propionitrile, l'acide acétique; ces bases se rangent en première approximation sur des horizontales lorsque l'on passe d'un milieu à l'autre (sauf pour l'acétonitrile). Le second groupe les alcools, l'éther éthylique, l'eau, le diméthylamino-4-azobenzène. Leurs positions dans l'acide trifluoroacétique, comparativement à celles qu'ils occupent dans l'acide acétique où les mélanges eau–acide sulfurique, indiquent que ces derniers composés présentent un caractère basique beaucoup moins affirmé (de 2 à 3 unités de pK). Certains gardent d'ailleurs un classement voisin dans les deux solvants de comparaison acide acétique et mélanges eau–acide sulfurique.

L'existence de liaisons hydrogène énergiques entre le groupement CF_3 fortement électronégatif et l'hydrogène de l'eau ou des alcools, etc., pourrait expliquer l'affaiblissement du caractère basique de ces composés dû à une solvatation renforcée des molécules protiques par le solvant CF_3COOH. Ceci serait d'ailleurs en accord avec les résultats obtenus pour des composés tels l'acétone, l'acétonitrile, le propionitrile, molécules aprotiques, dont la différence de basicité avec la chloro-4-nitro-2-aniline reste du même ordre de grandeur dans l'acide trifluoroacétique et l'acide acétique.

L'acide acétique devrait présenter, comme les alcools, un caractère basique moins affirmé dans l'acide trifluoroacétique alors que l'éther diéthylique devrait se comporter comme les bases telles que l'acétone. Or, ces résultats ne sont pas confirmés par l'expérience. Cela revient à supposer que le mode de solvatation de ces molécules et des cations correspondants est assez différent de celui correspondant aux composés précédents. Il est nécessaire de préciser que la force des liaisons hydrogène F...H n'est pas de même intensité pour toutes les molécules, et qu'il suffit qu'elle soit du même ordre pour la molécule B et le cation BH^+ correspondant pour que la basicité de B ne soit pas modifée. C'est probablement le cas pour l'acide acétique dans l'acide trifluoroacétique.

La comparaison du classement des bases dans l'acide trifluoroacétique avec celui donné sur l'échelle pK_{H_2O} conduit à faire quelques remarques. D'abord, l'eau est un milieu trop basique pour que l'on puisse y déterminer directement le pK des bases considérées. La position de ces bases figurant sur l'échelle pK_{H_2O} a été déterminée principalement dans les mélanges eau–acide sulfurique. Beaucoup de ces valeurs ont été en première approximation confirmées par des déterminations dans d'autres solvants. Il en est d'autres, par contre, telle celle relative à l'acétonitirile, qui traduisent un comportement particulier de certaines espèces dans les mélanges eau–acide sulfurique et que l'on ne retrouve pas lorsque l'on change de solvant. Comme l'échelle pK_{H_2O} devrait, en fait, rendre compte d'un classement indépendant de la nature du solvant, il nous a paru plus logique d'attribuer à l'acétonitrile un pK_{H_2O} égal à -4.2 déterminé dans l'acide acétique, celui du propionitrile étant du même ordre de grandeur.

En conclusion, le classement des bases ne donnant pas de liaisons hydrogène est sensiblement le même sur l'échelle pK_{H_2O} et dans l'acide trifluoroacétique, les bases R–OH pouvant voir leur caractère basique diminuer de 2 à 3 unités de pK selon les cas.

TABLEAU III

VALEURS p$K_{HA}-$pK_{HCl} RELATIVES À DIVERS ACIDES HA DANS L'ACIDE TRIFLUOROACÉTIQUE, L'ACIDE ACÉTIQUE, L'ACIDE FORMIQUE, L'ÉTHANOL ET L'EAU

Acides HA	*CF_3COOH*	*CH_3COOH*	*HCOOH*	*CH_3CH_2OH*	*H_2O*
Perchlorique	-4.0				
Sulfurique	-2.3	-1.0[20]	-0.8[34]		
Chlorosulfonique	-2.2				
Méthanesulfonique	-1.7	-0.5[20]			
p-Toluène sulfonique	-1.5	-0.5[20]			
Bromhydrique	-1.2	-1.8[20]		-0.4[2]	-2.4[29]
Fluoborique	-0.8				
Iodhydrique	-0.8				
Chlorhydrique	0	0	0	0	
Nitrique	$>+2$	$+1.8$[20]			

TABLEAU IV

pK_{H_2O} DES DIVERS ACIDES HA MESURÉS DANS L'ACIDE TRIFLUOROACÉTIQUE
(Le pK_{H_2O} de l'acide chlorhydrique[2] a été pris comme référence)

Acides HA	*pK_{H_2O}*
Perchlorique	-7.7
Sulfurique	-6.0
Chlorosulfonique	-5.9
Méthanesulfonique	-5.4
p-Toluène sulfonique	-5.4
Bromhydrique	-5.2
Fluoborique	-4.9
Iodhydrique	-4.9
Chlorhydrique	-3.7
Nitrique	-1.3

CLASSEMENT DE LA FORCE DES ACIDES

Les acides étudiés sont forts dans l'eau. Pour pouvoir les différencier, il est nécessaire d'utiliser des milieux moins basiques que l'eau, ou bien de basicité équivalente, mais de faible constante diélectrique.

On rencontre en pratique deux types de solvants: les uns protoniques, tels CH_3COOH, CF_3COOH, HCOOH, EtOH, H_2O qui sont doués généralement de bonnes propriétés solvatantes vis-à-vis des substances minérales, les autres aprotoniques tels CH_3CN, CH_3NO_2, DMSO, qui, bien que bons solvants, donnent lieu souvent à des phénomènes d'association complexes, l'acide HA envisagé ne se dissociant plus en H^+ et A^- mais en donnant des ions condensés du type HA_2^-[28]. Le mode de dissociation étant différent, il est difficile alors d'effectuer des comparaisons avec les milieux où les associations sont peu fréquentes.

La comparaison du classement de la force des acides dans les différents solvants est nécessairement limitée étant donné le nombre restreint de résultats expérimentaux dont on dispose.

L'étude de la fonction de HAMMETT dans les mélanges eau–acide permet de donner un classement qualitatif de la force des acides totalement dissociés à l'état dilué, dans l'eau. On a par ordre de force décroissante $HClO_4 > H_2SO_4 > HBr > HCl > HNO_3$. Des mesures de tension de vapeur dans les mélanges H_2O–HCl, H_2O–HBr, H_2O–HI conduisent à des valeurs de pK_{H_2O} pour ces divers acides, égales respectivement[29] à -7, -9, -10. Elles ne sont qu'approchées. Des déterminations par résonance magnétique nucléaire donnent des valeurs de pK_{H_2O} assez différentes pour les mêmes acides. Ceci est principalement dû aux insuffisances de la méthode de mesure[30]. Par contre, les résultats obtenus dans les solvants moins basiques que l'eau, tel l'acide acétique, l'acide formique, ou l'éthanol, sont beaucoup plus précis.

L'ordre qualitatif précédent déterminé dans les mélanges eau–acide est conservé dans l'acide trifluoroacétique, partiellement dans l'acide acétique où une interversion entre les acides bromhydrique et sulfurique a été observée. Le peu de données dont on dispose dans les autres solvants est en accord avec les résultats obtenus dans les mélanges eau–acide (Tableau III et IV).

Les acides chlorosulfonique et iodhydrique, supposés plus forts que l'acide perchlorique[20] se comportent en fait dans l'acide trifluoroacétique comme des acides beaucoup plus faibles. Le fait que l'acide iodhydrique ne serait que partiellement ionisé dans l'acide acétique[31] et dans l'éthanol[32] confirme les résultats obtenus dans l'acide trifluoroacétique. On doit noter la position inattendue de l'acide iodhydrique dans l'acide trifluoroacétique, qui paraît moins fort que l'acide bromhydrique, contrairement à ce qui se passerait dans l'eau, dans l'acide acétique et probablement dans l'éthanol. Cette position indique que l'ion iodure aurait des propriétés basiques non négligeables dans l'acide trifluoroacétique, ce qui est en partie confirmé par les résultats de CADDY ET HARA constatant une transformation partielle des iodures en trifluoroacétates sous balayage d'azote[33].

Les positions de l'acide nitrique sur les échelles acide–base de l'acide acétique et de l'acide trifluoroacétique ne sont pas définies avec précision.

Finalement les couples $HA|A^-$ voient leur force relative approximativement conservée lorsque l'on compare des milieux tels que CF_3COOH, EtOH ou CH_3COOH. On ne met pas en évidence une variation importante de la position d'un couple $HA|A^-$

dans l'acide trifluoroacétique par rapport aux autres milieux considérés, comme dans le cas des couples $BH^+|B$ tel que $EtOH_2^+/EtOH$.

Nous tenons à exprimer nos remerciements à Madame Badoz-Lambling, Directeur de Recherches au C.N.R.S. pour l'intérêt qu'elle a bien voulu porter à cette étude.

RÉSUMÉ

Le classement de la force relative de 25 bases non chargées dans l'acide trifluoroacétique est comparé avec ceux établis dans l'acide acétique et les mélanges eau–acide sulfurique. Le pK_{H_2O} des acides suivants, forts dans l'eau, a été déterminé: acides perchlorique (−7.7), sulfurique (−6.0), chlorosulfurique (−5.9), méthanesulfurique (−5.4), *p*-toluène sulfonique (−5.4), bromhydrique (−5.2), fluoborique (−4.9), iodhydrique (−4.5), chlorhydrique (−3.7), et nitrique (−4.3).

SUMMARY

The classification of the relative strengths of 25 uncharged bases in trifluoroacetic acid is compared with those established in acetic acid and water–sulphuric acid mixtures. The pK_{H_2O} values of the following acids, which are strong in water, have been determined: perchloric acid, −7.7; sulphuric acid, −6.0; chlorosulphuric acid, −5.9; methanesulphuric acid, −5.4; *p*-toluenesulphonic acid, −5.4; hydrobromic acid, −5.2; fluoroboric acid, −4.9; hydroiodic acid, −4.5; hydrochloric acid, −3.7; nitric acid, −4.3.

ZUSAMMENFASSUNG

Die Reihenfolge der relativen Stärke von 25 ungeladenen Basen in Trifluoressigsäure wird mit den in Essigsäure und Wasser–Schwefelsäure-Gemischen festgestellten Werten verglichten. Die pK_{H_2O}-Werte der folgenden in Wasser starken Säuren sind bestimmt worden: Perchlorsäure (−7.7), Schwefelsäure (−6.0), Chlorsulfonsäure (−5.9), Methansulfonsäure (−5.4), *p*-Toluolsulfonsäure (−5.4), Bromwaserstoffsäure (−5.2), Fluorborsäure (−4.9), Jodwasserstoffsäure (−4.5), Chlorwasserstoffsäure (−3.7) und Salpetersäure (−4.3).

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DETERMINATION OF SOLUBLE CARBOHYDRATES IN SEA WATER BY PARTITION CHROMATOGRAPHY AFTER DESALTING BY ION-EXCHANGE MEMBRANE ELECTRODIALYSIS

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Reliable methods of characterizing and estimating quantitatively different soluble sugars in sea water do not seem to have been developed, although the presence of dissolved carbohydrates has been shown[1-6]. With a suitable method it would be possible to achieve a better understanding of the microbiological life in the sea and even the effect on the marine environment of human activities.

Since the concentration of soluble carbohydrates in sea water is so low (of the order of $\mu g\ l^{-1}$ for each species) it is necessary to isolate them from the sea salts. Isolation techniques have been investigated by JEFFREY AND HOOD[7] and later by BADER *et al.*[8]. They used a ^{14}C-labelled aged algae culture, grown in the laboratory in fertilized sea water to produce dissolved organic compounds. After filtration with Millipore HA (0.45 μm) filters, they tested different methods such as dialysis, electrodialysis with different types of membranes, carbon adsorption, coprecipitation with iron(III) hydroxide, solvent extraction and ion-exchange deionization. They pointed out the difficulties in the quantitative isolation of the organic compounds by these methods. Many compounds, especially carbohydrates, are easily digested by bacterial action. Some of the isolation procedures may cause decomposition and rearrangements of the organic constituents.

DEGENS *et al.*[9] tried a combination of evaporation and extraction with 80% ethanol of the acidified residue followed by ion-exchange desalting to isolate sugars and amino acids from sea water off the coast of California. In this investigation, they found five different monosaccharides, using one-dimensional descending paper chromatography. The quantitative determination was made by visual comparison with synthetic standards, run on the same sheet. The precision in the final stage was about ±15%. The isolation procedure however, may cause drastic changes in the organic constituents.

Ion retardation with Retardion 11 A8 was used by SCHAEFER[10] to desalt sea water. This resin is an amphoteric polystyrene, polyacrylate ion-exchanger of so-called "snake cage" type. The ion-exchanger has negative charges ($-COO^-$ from polyacrylic acid), trapped inside a network polymer with charges of the opposite sign ($-R_3N^+$ from Dowex 2-X8). Such a resin swells in water by hydration and absorbs salts much more strongly than non-electrolytes. Thus a column with Retardion 11 A8 will hold back dissolved salts allowing non-electrolytes to emerge from the column first. The separation is especially efficient with rather large molecules of hydrophilic nature such as sugars. With this method it was possible to remove 90%

of the inorganic salts from the "organic fraction" by a one-step procedure. The advantage of this method compared with combined anion and cation ion-exchange is that no regeneration is necessary. It was not possible, however, to remove sulphates completely from the sugars. Our experience in working with low concentrations of glucose in standard sea water is that the desalination is not effective enough, and after evaporation of the eluate it was not possible to retrieve the glucose in the salt residue.

JEFFREY AND HOOD[7] did not report any results from electrodialysis with ion-exchange membranes, but state: "It is believed that under controlled conditions with respect to current, time and membrane arrangement, this technique has unrealized capabilities for the separation of certain organic compounds", *i.e.* from salts.

Demineralisation of sugar solutions was carried out by ANDERSON AND WYLAM[11]. They used electrodialysis with ion-exchange membranes successfully without any loss of sugar and stated that the use of ion-exchange membranes in an electrodialysis cell has definite advantages over other kinds of membranes. Furthermore, they showed that the membranes are impermeable to saccharides and therefore complete recovery of sugars could be obtained from electrodialysed solutions. On the basis of this information a study of desalting by ion-exchange membrane electrodialysis was undertaken in this laboratory; low concentrations of carbohydrates in standard sea water were used, and an apparatus was constructed to fit these conditions. Two methods were used for the quantitative analysis of the sugars in the desalted and evaporated sea water sample, gas–liquid chromatography and liquid–liquid chromatography.

EXPERIMENTAL

Apparatus

The technique of ion-exchange membrane electrodialysis has been described by various workers[12–15].

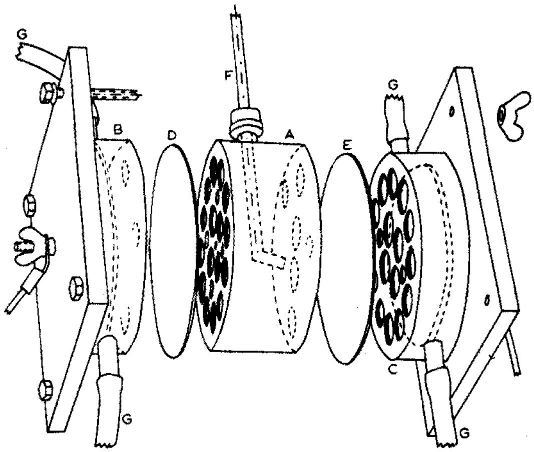


Fig. 1. Exploded view of electrodialysis apparatus. (A) Center compartment for sea water; (B) and (C) anode electrode and cathode electrode compartment; (D) and (E) Permaplex A-20 and Permaplex C-20 ion-exchange membranes; (F) stirrer; (G) flow of tapwater.

The electrodialysis cell used in this work was arranged (see Fig. 1) with three circular compartments. The inner "plexiglas" (Röhm & Haas) walls of the outer compartments and the walls of the inner compartment had matched holes of various sizes (5–20 mm in diameter). The outer walls of the outer compartments consisted of 10 mm thick, 16 × 16 cm square (Plexidur) (Röhm & Haas) plates. The diameter of the compartments was 12 cm and the volume of the inner compartment was 430 cm^3. A second unit has been constructed which holds 2.2 l of sea water. The carbon electrodes were so placed in the outer compartments that they could be cooled by a flow of tap water. The membranes were placed between the compartments, which were pressed together with four screws between the outer "plexidur" plates. Thereby the membranes function as packings, preventing the leakage of both the inner sea-water sample and the outer cooling water.

Membranes

The membranes were Permaplex C-20 and Permaplex A-20 (Permutit Co., Ltd.). These are made of milled synthetic ion-exchange beads with a binder, such as polythene, and extruded in the form of flexible extended sheets. Permaplex C-20 is a cation-selective membrane containing highly ionized sulphonic groups. Permaplex A-20 is an anion-selective membrane containing quaternary ammonium groups. In the fully swollen state they are about 1 mm thick and have very good mechanical strength. The anion-exchange membrane is resistant to attack by chlorine from the anode. The membranes were developed for use in electrolytic cells for removal of ions by electro-osmosis and are therefore permeable to ions of one charge and largely impermeable to ions of opposite charge. They are arranged (see Fig. 1) so that positively and negatively charged ions can pass through the membrane into the cathode and anode compartments respectively.

Power supply

The power supply was a d.c. stabilizer Philips G.M. 455 B which delivers 250 mA at 500 V of direct current. A new power supply which delivers 5 A at 250 V has been constructed.

Electrodialysis cell data

Sea-water sample volume:	430 cm^3
"Effective" membrane surface:	52 cm^2
Current density	5 mA cm^{-2}
Desalting time for 0.5 *M* sodium chloride:	24 h

Sampling of sea water

The sea-water samples were collected from two stations: inside and outside the threshold of the Gullmarfjord on the Swedish west coast. At each station, one sample was taken from the surface layer ($S=24^0/_{00}$) and one from a depth of 35 m ($S=35^0/_{00}$) below the halocline. The water was immediately disinfected with mercury chloride and filtered through a Millipore HA filter with a pore size of 0.45 μm.

Procedure

The sea water was placed in the center compartment of the apparatus. All the membranes had been soaked and washed before use. A maximum current of 250 mA at a potential of 90 V was applied across the membranes for 24–30 h, depending on the salinity of the sea water (20–35‰). During the electrolysis the potential was increased stepwise to 500 V to maintain a current of 250 mA. At the end of the desalting procedure the current dropped to zero. After desalting, the water was evaporated nearly to dryness at 15 mm Hg and 40°. The residue was then dissolved in 2 ml of 85% ethanol for subsequent analysis by partition chromatography (see below).

Control of salt content

The salt content in the desalted sample was checked in three ways: (*a*) sodium content by atomic absorption spectroscopy, (*b*) conductivity measurements (can also be seen from the current meter on the power supply), (*c*) silver nitrate for the chloride content.

Control of sugar loss

The loss of sugar was studied by a radiochemical technique with D-glucose uniformly labelled with carbon-14 (Radiochemical Centre, Amersham, England). The specific activity was 3.1 mCi mmol^{-1} (17.0 μCi mg^{-1}) of glucose. The β-radioactivity was measured with a windowless, gas flow proportional counter (Nuclear Chicago).

A stock solution was prepared by dissolving 29 mg of D-glucose-^{14}C in 1 l of redistilled water; 10 ml of this solution was diluted with 400 ml of redistilled water. This solution was placed in the middle compartment of the ion-exchange membrane electrodialyzer in the same way as the sea-water samples. A voltage of 200 V was applied for 44 h; 1-ml samples were taken periodically and dried on a planchet for β-counting.

Partition chromatography

The desalted and evaporated sample was dissolved in 2 ml of 85% ethanol. The carbohydrates were then separated by partition chromatography on an ion-exchange column by a method devised by SAMUELSON *et al.*[16,17] with 85% ethanol as the eluant. The column separates saccharides efficiently and the sugars in the eluate were automatically determined in a Technicon Auto-Analyzer by means of an orcinol method. Improvements in this method are being made and will be reported separately.

RESULTS AND DISCUSSION

The desalting procedure

The desalting procedure is highly efficient and no detectable amounts of sodium or chloride can be found. Upon evaporation a small residue is obtained, and this residue may contain other dissolved organic matter than sugars.

The results of the radiochemical determination of the loss of D-glucose-^{14}C are presented in Fig. 2. It can be seen that a slight drop of activity occurs at the beginning, but thereafter the activity is constant. The scatter is most likely due to the difficulty in preparing uniform samples. After 44 h, the remainder of the water, 388 ml (410 ml minus eleven 2-ml samples), was evaporated in the same way as the sea-water samples to 10 ml; 1 ml of this residue was measured for β-activity yielding an activity of 133.500 counts per 18 sec. From the calibration curve which showed that no correction for dead-time was needed, the glucose loss can be calculated as 11% (133.500 out of 158.500 × 410/388) after corrections for decreased volume.

There is a great advantage with this desalting method which depends on the fact that these sugars are neutral and that they are not influenced to any great extent by the electrical field in the solution. There is no danger of hydrolysis or epimerisation of the sugars since the exchange sites of the membranes are not occupied by hydrogen or hydroxyl ions. Unlike the conventional ion-exchangers, the membranes do not require any chemicals for periodic regeneration, because desalting is continuously effected by means of electric power. The time necessary for the desalting operation, in the present case 24–30 h depending on the salinity of the sea water, can easily be reduced with a more powerful rectifier. There is a maximum d.c. voltage or power input for maximum desalting speed depending on the cooling of the electrodes, the gas evolution and the decomposition of the water that can affect the membranes.

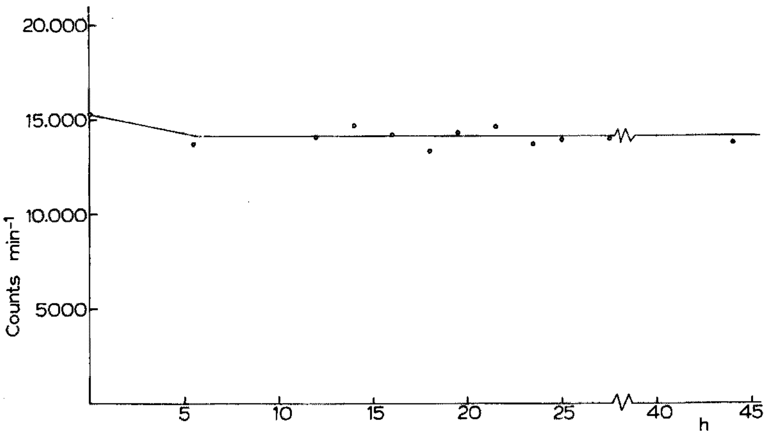


Fig. 2. Activity measurements of ^{14}C-glucose (0.7 μg ml^{-1}) during electrodialysis with a voltage of 200 V applied for 44 h.

The reduction in bacterial count observed in electrodialysis has been reported to be caused by electrophoretic deposition on the surface of the membranes and is favourable for sugar analysis[5]. The sea water is disinfected, of course, but the mercury chloride is removed during the desalting process. The sea-water compartment is closed during the desalting, however, which protects the sugars from bacterial attacks.

Partition chromatography

Partition chromatography on anion-exchange resins in their sulphate form with aqueous ethanol as eluant is a useful tool in the separation of most monosaccharides of biological origin. The results are presented in Fig. 3 and Table I. The percentage error is certainly less than 10% and can probably be lowered to 1%.

Several of the monosaccharides have not previously been found in sea water, but they can now be determined quantitatively. In addition to the monosaccharides presented in Table I, there were indications in some samples of small amounts of fucose and sorbose. The coastal water region in the Gullmarfjord is complicated and no far-reaching conclusions should be drawn from these few results, which show only the merits of the method.

Chromatographic separation of carbohydrates on cation-exchange resins in the lithium form, confirmed the presence of the reported sugars separated with the anion-exchanger. In addition to the monosaccharides, indications were found that ethylene glycol, glycerol and sucrose were also present. The sample was run in a manner similar to that used with the anion-exchanger partition column. Ethylene glycol and glycerol were determined by acidified periodate oxidation instead of the orcinol method.

Gas–liquid chromatography

Problems arose in the gas chromatographic determination of the sugars from sea water which could not be solved in a satisfactory way. Sugars isolated and dried

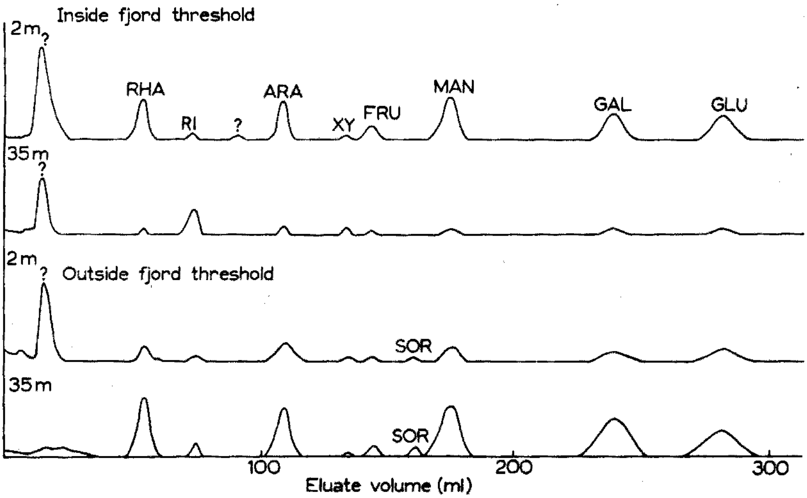


Fig. 3. Liquid–liquid partition chromatogram with anion-exchange column in the sulphate form. Concentrations evaluated from the peak areas are given in Table I.

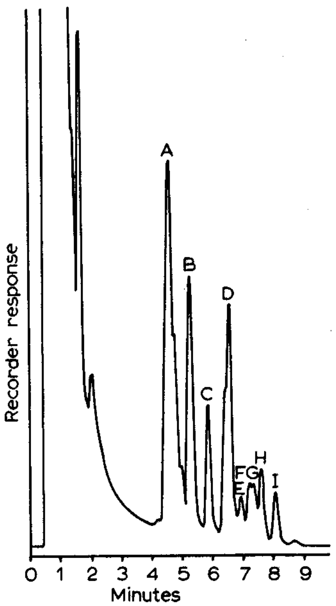
TABLE I

THE DETERMINATION OF MONOSACCHARIDES IN THE GULLMARFJORD BY LIQUID–LIQUID PARTITION CHROMATOGRAPHY

(All results are given as $\mu g\ l^{-1}$)

	Inside threshold at a depth of		*Outside threshold at a depth of*	
	2 m	*35 m*	*2 m*	*35 m*
Rhamnose	20.5	3.0	5.9	25.2
Ribose	1.0	8.1	0.6	2.8
Arabinose	11.5	3.8	3.9	14.7
Xylose	0.5	2.7	0.3	<0.15
Fructose	14.3	1.2	2.0	2.9
Mannose	29.8	2.7	9.9	32.6
Galactose	32.5	2.7	8.7	37.8
Glucose	46.5	9.3	13.3	32.5

from 2 l of sea water were silylated to trimethylsilylethers[18-28]. The conversion of the carbohydrates to ethers was made with N-trimethylsilylimidazole in pyridine (1.5 meq ml^{-1}). This reagent is the most rapid and powerful silylating agent reported for hydroxyl groups and the reaction is quantitative[28]. It is said[29] that N-trimethylsilylimidazole causes less anomerization than does hexamethyldisilazane and trimethylchlorosilan in pyridine. As can be seen from the chromatograms in Figs. 4 and 5, a number of anomerization peaks appeared and severe overlapping occurred. It is not possible to separate all the peaks on the same column and therefore two columns with stationary phases of different polarity were used. The non-polar phase was 3% OV-1 on (80–100 mesh) Chromosorb W(HP) (Fig. 4) and the mildly polar phase was 3% OV-17 on (80–100 mesh) Chromosorb W(HP)(Fig. 5). The separation was done on a Perkin-Elmer 881 dual-column gas chromatograph fitted with a hydrogen flame ionisation detector. The samples were run with temperature programming, 10° min^{-1}, on coiled glass columns with nitrogen as carrier gas and a flow rate of 20 ml min^{-1}. Because of serious overlapping of the different anomers, it was not possible in all cases to identify the form of mutarotation. Overlapping also prevented the identification of arabinose.



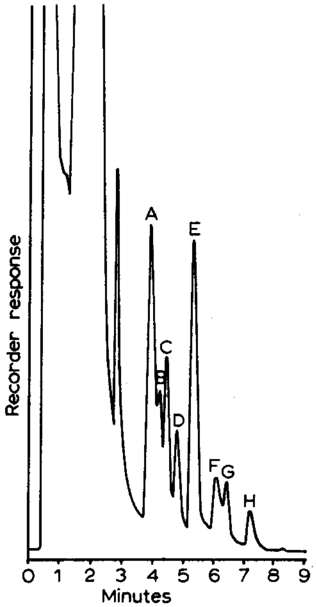


Fig. 4. Gas–liquid chromatograms of the TMS monosaccharides isolated from sea water on 6′ × $\frac{1}{4}$″ glass columns. The column used was nonpolar OV-1 with an initial temperature of 135° and programmed for a temperature increase of 10° min^{-1}. The carrier gas flow of nitrogen was 20 ml min^{-1}. The components are: (A) rhamnose 1, ribose 1 and ribose 2; (B) rhamnose 2; (C) xylose; (D) fructose, mannose 1 and galactose 1; (E) galactose 2; (F) mannose 2; (G) galactose 3; (H) glucose 1; (I) glucose 2.

Fig. 5. Gas–liquid chromatograms of the TMS monosaccharides from the same sample as in Fig. 4. The conditions were the same but mildly polar columns OV-17 were used. The components are: (A) rhamnose 1, xylose 1; (B) ribose; (C) rhamnose 2; (D) fructose; (E) mannose 1, galactose 1; (F) galactose 2; (G) glucose 1, galactose 3; (H) glucose 2.

Gas–liquid chromatography methods cannot be used properly as a quantitative procedure for carbohydrates in sea water. There are too many carbohydrates with complex biological origin. Reduction of sugars to sugar alcohols reduces the number of multiple peaks caused by anomerization[30], but the loss of material by reduction is considerable, and some sugars are reduced to the same alcohol (*e.g.* sorbose and glucose both give sorbitol). Furthermore, the separation of hexitols is very poor[18,21].

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SUMMARY

A method for the determination of different soluble sugars in sea water is discussed. An apparatus for desalting the sea water by electrodialysis with ion-exchange membranes is described. The desalted samples are evaporated *in vacuo* and investigated by liquid–liquid and gas–liquid chromatographic methods. These methods are compared and the former is shown to be superior for the determination of different sugars. With the liquid–liquid partition chromatographic method, eight monosaccharides were determined in the range of 0.15–46.5 $\mu g\ l^{-1}$; small amounts of sorbose, fucose, sucrose, ethylene glycol and glycerol were also detected.

RÉSUMÉ

Une étude est effectuée sur le dosage de différents sucres solubles dans l'eau de mer. On décrit un appareil pour désaler l'eau de mer par électrodyalise avec des membranes échangeuses d'ions. Les échantillons désalés sont évaporés au vide et examinés par des méthodes chromatographiques liquide–liquide et gaz–liquide. Par la méthode chromatographique de partage liquide–liquide, on a pu doser huit monosaccharides à des concentrations de 0.15 à 46.5 $\mu g\ l^{-1}$; de failles teneurs de sorbose, fucose, sucrose, éthylèneglycol et glycérol peuvent être également détectées.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur Bestimmung verschiedener löslicher Zucker in Meerwasser erörtert. Eine Apparatur für die Entsalzung von Meerwasser durch Elektrodialyse mit Ionenaustauschmembranen wird beschrieben. Die entsalzten Proben werden im Vakuum eingedampft und mit Methoden der Flüssig–Flüssig- und Gas–Flüssig-Chromatographie untersucht. Diese Verfahren werden miteinander verglichen; das erstere ist für die Bestimmung verschiedener Zucker besser. Mit der Flüssig–Flüssig-Verteilungs-chromatographie wurden acht Monosaccharide im Bereich 0.15–46.5 $\mu g\ l^{-1}$ bestimmt; kleine Mengen von Sorbose, Fucose, Sucrose, Äthylenglykol und Glycerin wurden ebenfalls nachgewiesen.

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ENZYMATIC METHODS OF ANALYSIS

TRACE ANALYSIS OF VARIOUS PESTICIDES WITH INSECT CHOLINESTERASES

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Many workers have reported enzymatic determination of pesticides. GUILBAULT AND KRAMER[1,2] used both lipase and cholinesterase enzymes to determine very low concentrations of certain pesticides. GIANG AND HALL[3] used acetylcholine chloride as substrate for cholinesterase to measure the percentage inhibition by organophosphorus insecticides. Although these papers and many more provide sensitive methods of analysis, the major emphasis has been on organophosphorus compounds. Moreover, these methods lack specificity. GUILBAULT *et al.*[2,4], have already reported inhibition of lipase by chlorinated insecticides such as Aldrin, Lindane, Heptachlor, DDT, and a carbamate, Sevin. A sensitive method for analysis of all the above-mentioned insecticides in addition to bismuth, beryllium and Methylparathion, has been proposed[4]. Unfortunately, these methods are of limited use because of a lack of specificity.

Since it is known that various animals and insects respond in different ways to different insecticides or pesticides, it seemed desirable to isolate a more purified enzyme from different sources for studying their inhibition by different pesticides. With these facts in mind, inhibitory studies of partially purified cholinesterases from housefly (DDT-resistant), housefly (NAIDM), sugar boll weevil, fire ant and German cockroaches, by various pesticides were conducted.

EXPERIMENTAL

Reagents

Substrate. N-Methylindoxyl acetate (Isolab, Inc., Drawer 4350, Akron, Ohio). A 10^{-2} *M* solution (1.91 mg ml^{-1}) was prepared in methyl cellosolve.

Pesticides. Stock solutions or various concentrations were prepared in dioxane. The pesticides were all 99+% purity and were all obtained from Polyscience Corp., Evanston, Illinois, except for Paraoxon which was obtained from American Cyanamid Co. (Bound Brook, N. J.). The Paraoxon content of Parathion was assayed by i.r. spectroscopy ($P \rightarrow O$ bond) and thin-layer chromatography, and was found to be about 1%.

Buffers. 0.1 *M* Phosphate buffer was prepared by dissolving sodium dihydrogen phosphate in triply distilled water. The pH was adjusted to 7.0 with sodium hydroxide.

Procedures

Measurement of enzyme activity. Cholinesterase activity of different preparations for various studies was assessed either fluorimetrically, colorimetrically, or titrimetrically. The inhibitory effect of pesticides on enzyme activity was determined fluorimetrically[5,6] with N-methylindoxyl acetate as substrate. The substrate preference studies were done titrimetrically by continuous titration wlth a Metrohm 3M titrator. As a rule the total volume of the reaction mixture was 10 ml. Generally, 3ml of 0.2 *M* magnesium chloride, 1 ml of 0.05 *M* TRIS buffer, 4 ml of distilled water and 1 ml of properly diluted enzyme solution were pipetted into the reaction vessel and brought to pH 7.4 with sodium hydroxide; 1 ml of substrate, which was previously adjusted to pH 7.4 with sodium hydroxide, was then added to start the reaction. The amount of hydroxide consumed *vs.* time was recorded after a constant rate had been attained. The enzymatic hydrolysis of acetylcholine was spot-checked by the modified method of SIMPSON *et al.*[7]. One enzyme unit is reported as one micromole of substrate hydrolyzed per minute for all the methods used in this experiment.

Assay of pesticides. In a previous study[6], N-methylindoxyl esters were found to be the best substrates for the assay of cholinesterase, from considerations of stability, blank rate, rate of enzyme hydrolysis, and lowest detectable enzyme concentration. Inhibitory studies on enzyme activity were therefore performed using the fluorogenic substrate N-methylindoxyl acetate, which is rapidly cleaved by cholinesterase to the highly fluorescent N-methylindoxyl.

A 10^{-2} *M* solution of N-methylindoxyl acetate was prepared in methyl cellosolve and used as substrate for each cholinesterase (overall concentration in solution, $3 \cdot 10^{-4}$ *M*). The other conditions for assay (buffer, pH, etc.) were the same as previously found optimal[6]. The rate of production of the highly fluorescent N-methylindoxyl from the non-fluorescent ester N-methylindoxyl acetate was measured at a $\lambda_{ex} = 430$ nm and a $\lambda_{em} = 501$ nm. The concentration of each enzyme was selected with regard to its activity and the rate of increase of fluorescence. Since their activities were not the same, a different concentration of each enzyme was picked which gave an appropriate rate. All concentrations were, however, taken from the linear portion of the curve drawn by plotting $\Delta F/\Delta T$ *vs.* enzyme concentration. The blank rate, *i.e.* rate without any pesticide present, was always taken by adding 0.1 ml of dioxane, the solvent for pesticides.

To 3.0 ml of 0.1 *M* phosphate buffer pH 7. 0, and 0.1 ml of 10^{-2} *M* N-methylindoxyl acetate was added 0.1 ml of dioxane (the solvent used for the pesticides). The fluorescence was adjusted to zero and then 0.1 ml of the appropriate enzyme stock solution was added. The rate of change in fluorescence with time, ΔF min^{-1}, was recorded. This rate was labelled as the blank rate or the rate with no pesticide present. To 3.0 ml of buffer was added 0.1 ml of a solution of the pesticide to be assayed and the fluorescence was adjusted to zero. Then 0.1 ml of the enzyme solution was added and ΔF min^{-1} recorded. The percent inhibition was calculated as below:

$$\%\ \text{Inhibition} = \frac{(\Delta F\ \text{min}^{-1})_{\text{No Inhibition}} - (\Delta F\ \text{min}^{-1})_{\text{Inhibition}}}{(\Delta F\ \text{min}^{-1})_{\text{No Inhibition}}} \times 100$$

The concentration of pesticide was determined from a calibration plot of % inhibition *vs.* concentration of the pesticide. The rate of production of fluorescence was proportional to the concentration of enzyme as affected by the pesticide present.

Electrophoresis. Disc electrophoresis was accomplished with acrylamide gel cast in glass tubes[8]. The applied current was maintained at 3 mA per column until the dye front approached 3 mm from the end of the column. Cholinesterase activity was detected with N-methylindoxyl acetate as substrate[6].

Estimation of protein. Protein concentrations in different preparations were estimated by the method of Folin-Ciocaltau as outlined by LITWACK[9] with egg albumin as reference. The specific activity of the preparation was calculated based on the enzyme units per mg of protein obtained by this method.

Source and purification of cholinesterase. The insects used were of mixed sexes and were selected at random from an insecticide-susceptible wild species with the exception of DDT-resistant houseflies. Houseflies (both NAIDM and DDT-resistant), and German cockroaches were obtained from the National Communicable Disease Center, Atlanta; the fire ants were collected at a U. S. Department of Agriculture fire-ant farm, Gulfport, Mississippi, and the sugar boll weevils were collected at a farm of the Entomology Department, Louisiana State University, Baton Rouge. These insects were reared in the laboratory by the usual procedures. The method of cholinesterase preparation was exactly the same as described previously[10].

RESULTS AND DISCUSSION

The purity of the cholinesterase preparations from different insects is shown in Table I and Fig. 1.

As can be seen, the specific activity of these preparations ranged from 4–30. The low specific activity obtained with sugar boll weevil enzyme was due to the

TABLE I

THE SPECIFICITY OF PARTIALLY PURIFIED INSECT CHOLINESTERASES

Insect	*Fire ants*	*Housefly (DDT-resistant)*	*Housefly (NAIDM)*	*Cockroaches*	*Sugar boll weevils*
Protein $\mu g\ ml^{-1}$	138	162	174	145	97
Enzyme Activity (Units)	2.14	4.94	2.80	3.95	0.38
Specific Activity	15.5	30.5	16.1	27.2	4.0

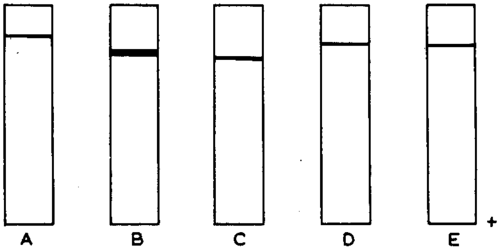


Fig. 1. Electrophoretic migration of different insect cholinesterases in polyacrylamide gel after 5-min incubation with N-methylindoxyl acetate at pH 7.0. (A) Fire ant, (B) housefly (DDT-resistant), (C) housefly (NAIDM), (D) German cockroaches, (E) sugar boll weevils.

gradual loss of activity during purification. The reason is not known. The large differences in specific activity between the two types of houseflies may be a result of either the change of genetic code for the enzyme synthesis or just a steric alteration of the enzyme molecule through the effect of the pesticides.

Preparations were further characterized by electrophoresis in polyacrylamide gel. Results (Fig. 1) indicated that these preparations were purified to a state of electrophoretic homogeneity. Therefore, the preparations thus obtained in this experiment appeared to be of adequate purity for this investigation.

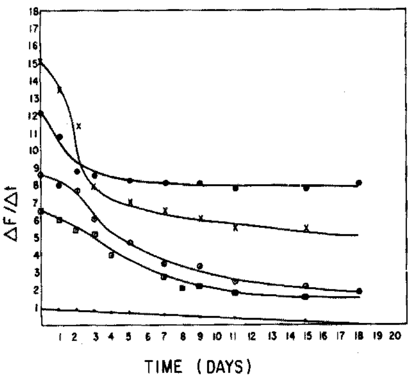
Preparations were characterized and classified by their substrate preference toward acetylcholine chloride, propionylcholine chloride, butyrylcholine chloride, and benzoylcholine iodide (Table II).

The difference in substrate preference between ChE from fire ant or housefly

TABLE II

HYDROLYSIS RATE FOR VARIOUS INSECT CHOLINESTERASES AGAINST DIFFERENT SUBSTRATES

Substrate	*Fire ant*	*Housefly (DDT-resistant)*	*Housefly (NAIDM)*	*Cockroaches*	*Sugar boll weevils*
Acetylcholine chloride	0.12	0.56	0.37	1.98	0.12
Propionylcholine chloride	0.63	1.03	0.84	1.76	0.11
Butyrylcholine chloride	0.98	2.12	1.11	0.84	0.02
Benzoylcholine chloride	0.23	0.76	0.31	0.02	0.00



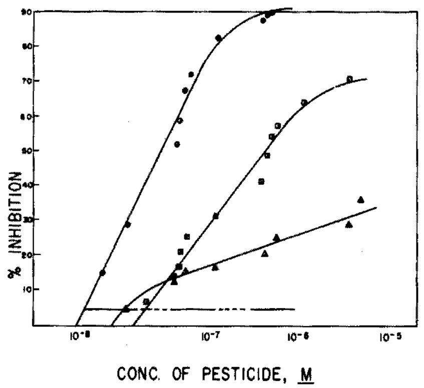
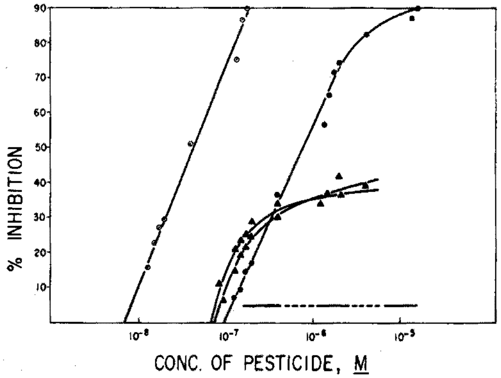


Fig. 2. Stability of purified insect cholinesterase preparations with time. Rate of hydrolysis of N-methylindoxyl acetate, ΔF min^{-1}, by the enzyme preparation used as measure of enzyme activity. (x) Housefly (DDT-resistant), (●) cockroaches, (⊙) housefly (NAIDM), (⊡) fire ant, (•) sugar boll weevil.

Fig. 3. Plot of % inhibition of fire-ant cholinesterase by various pesticides. 3-min preincubation. (⊙) DDVP; (⊡) Methylparathion; (▲) Parathion; (—...—) Aldrin, DDT, Dieldrin, Captan Dalapon, 2,4-D-Acid, Heptachlor, Lindane, Mirex, Methoxychlor, Sevin, Paraoxon.

and that from cockroaches or sugar boll weevils suggests that they are different enzymes. The differences in inhibitory effect of these enzymes against different pesticides again confirm this suggestion. The cholinesterase of fire ant and housefly appears to be a pseudo- or butyryl-cholinesterase, whereas the enzyme from cockroaches and sugar boll weevils is an acetylcholinesterase.

Data on the stability of various enzymes are shown in Fig. 2. The stability was determined by noting the rate of hydrolysis of N-methylindoxyl acetate in ΔF min^{-1}. The only enzyme which was fairly stable was that from German cockroach although during the first three days at 4° it also lost about 25% of its activity.



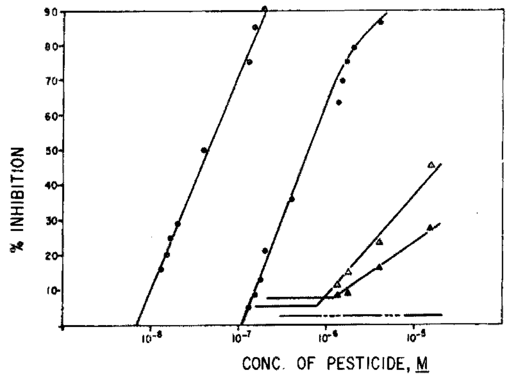
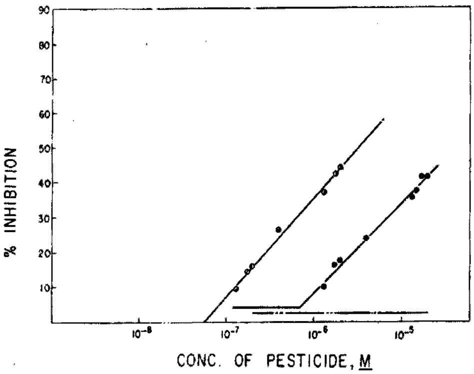


Fig. 4. Plot of % inhibition of housefly (NAIDM) cholinesterase by various pesticides. 3-Min preincubation. (⊙) DDVP; (●) Sevin; (▲) Parathion; (◬) Methylparathion; (—...—) Aldrin, Captan, Dalapon, DDT, Dieldrin, 2,4-D-Acid, Heptachlor, Lindane, Mirex, Methoxychlor.

Fig. 5. Plot of % inhibition of housefly (DDT-resistant) cholinesterase by various pesticides. 3-Min preincubation. (⊙) DDVP; (●) Sevin; (▲) Parathion; (◬) Methylparathion; (—...—) Aldrin, Captan, Dalapon, DDT, Dieldrin, 2,4-D-Acid, Heptachlor, Lindane, Mirex, Methoxychlor.



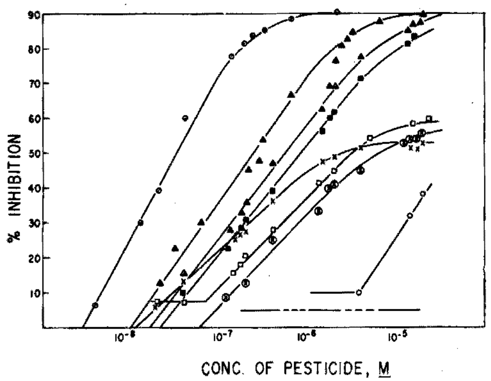


Fig. 6. Plot of % inhibition of sugar boll weevil cholinesterase by various pesticides. 3-Min preincubation. (⊙) DDVP; (●) Parathion; (—...—) Aldrin, Captan, Dalapon, DDT, Dieldrin, 2,4-D-Acid, Heptachlor, Lindane, Mirex, Methoxychlor, Methylparathion, Sevin.

Fig. 7. Plot of % inhibition of cockroach cholinesterase by various pesticides. 3-Min preincubation. (⊙) DDVP; (■) Sevin; (▲) Parathion; (◬) Methylparathion; (×) Aldrin; (⊗) Dieldrin; (○) Captan; (□) Heptachlor; (—...—) Dalapon, DDT, 2,4-D-Acid, Lindane, Mirex, Methoxychlor

TABLE III

I_{50} VALUES FOR VARIOUS CHOLINESTERASES
(— indicates that the I_{50} is greater than $1 \cdot 10^{-3}$ M or that inhibition does not reach 50%. × not investigated)

Enzyme Source	*Pesticide*						
	Paraoxon	*Parathion*	*Methylparathion*	*DDVP*	*Sevin*	*Aldrin*	*Heptachlor*
Housefly (DDT-resistant)	×	—	—	6.3×10^{-8} M	8.2×10^{-7} M	—	—
Housefly (NAIDM)	×	—	—	6.5×10^{-8} M	8.8×10^{-7} M	—	—
Sugar boll weevil	×	—	—	5.3×10^{-6} M	—	—	—
Fire ant	—	—	1.5×10^{-6} M	9.6×10^{-8} M	—	—	—
Cockroaches	3.2×10^{-8} M	2.0×10^{-7} M	7.3×10^{-7} M	4.8×10^{-8} M	9.3×10^{-7} M	5×10^{-6} M	6.0×10^{-6} M

More specificity in the assay of pesticides with enzymatic systems was observed. Fire-ant cholinesterase was specifically inhibited by DDVP, and Methylparathion (Fig. 3). Even Parathion had little effect on this enzyme. None of the other twelve inhibitors (Paraoxon, Aldrin, Captan, Dalapon, DDT, Dieldrin, 2,4-D-Acid, Heptachlor, Lindane, Mirex, Methoxychlor, and Sevin) inhibited it at all. Cholinesterase from both types of housefly (NAIDM and DDT-resistant strains) were specific for DDVP and Sevin and others had little or no effect up to 10^{-6} M concentration of the inhibitor (Figs. 4 and 5). Although not as sensitive as other cholinesterases, the sugar boll weevil was totally specific for DDVP below 10^{-6} M concentration (Fig. 6). Parathion interfered at concentrations greater than 10^{-6} M; paraoxon would probably also interfere. The enzyme from cockroaches was the most sensitive of all but lacked specificity. Although it was most sensitive to DDVP, Paraoxon, Parathion and Methyl-Parathion (Fig. 7), a good number of chlorinated insecticides, carbamates and herbicides inhibited it.

From the results of this study it can be concluded that in addition to the sensitivity (Table III), improved selectivity in the assay of pesticides by enzymatic methods was achieved.

It is known that phosphorothionates are not strong inhibitors of esterases but that their oxygen analogs are very potent inhibitors[11]. Since both Parathion and Methylparathion showed strong inhibition, as is clear from the I_{50} values, the presence of oxygen analogs (Paraoxon) as impurities was suspected. The i.r. spectra of both Parathion and Methylparathion had a very distinct peak corresponding to $-P=O$. Separation by thin-layer chromatography showed less than 1% impurity but I_{50} values were only *ca.* 10-fold less for pure Paraoxon. Hence it was concluded that inhibition was not only due to Paraoxon as impurity, but also to Parathion. Since both Parathion and Methylparathion, available commercially and in common use, are of 99% purity, the data of inhibition by these pesticides have been included above. Such data can be useful in qualitative and quantitative work. Moreover, it is very difficult to obtain absolutely pure Parathion or to purify this compound to remove the minute traces of Paraoxon impurity. It is also interesting to note that although both pure Paraoxon and 99% pure Parathion have very little effect on fire-ant cholinesterase, Methylparathion is a good inhibitor (Table III).

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SUMMARY

The effect of fifteen different pesticides including carbamates, chlorinated hydrocarbons and organophosphorus compounds on cholinesterase from housefly, sugar boll weevll, fire ant and German cockroaches is reported. Since the cholinesterase

from each source show different inhibition by various inhibitors, an increase in the specificity of enzyme systems for the determination of pesticides is possible.

RÉSUMÉ

On examine l'influence de quinze pesticides différents comprenant carbamates, hydrocarbures chlorés, et composés organophosphorés, sur les cholinestérases d'insectes. Une augmentation de specificité de systèmes d'enzymes est possible pour le dosage de pesticides.

ZUSAMMENFASSUNG

Es wird über den Einfluss von fünfzehn verschiedenen Pesticiden wie Carbamaten, chlorierten Kohlwasserstoffen und Organophosphorverbindungen auf Cholinesterase verschiedener Insekten berichtet. Da die Cholinesterase jeder Herkunft unterschiedlicht Inhibition durch verschiedene Inhibitoren zeigt, ist eine Zunahme in der Spezifität dieser Enzymsysteme für die Bestimmung von Pesticiden möglich.

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THERMAL DEHYDRATION OF SOME 8-QUINOLINOL CHELATE HYDRATES

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Although several investigations have been concerned with the properties of 8-quinolinol (oxine) chelates, little interest has been shown in the hydrated chelates themselves. The thermal stabilities of a number of chelate hydrates have been summarized by HOLLINGSHEAD[1], but these are, at best, to be considered no more than procedural decomposition temperatures. CHARLES *et al.*[2-4] reported the thermal stability and volatility of some di- and trivalent metal chelates of 8-quinolinol, but did not deal with the hydrates. The thermal dissociation of chelates containing an extra molecule of the chelating agent as a solvate have been extensively investigated by WENDLANDT *et al.*[5-8]. Thermal studies pertaining specifically to the hydrates were made by BORREL AND PARIS[9] on the copper, magnesium, zinc and nickel chelates of 2-methyloxine (2-methyl-8-quinolinol); these, however, were limited to correlation of structure with the procedural decomposition temperature.

The purpose of the present investigation is to present data on the thermal dehydration of the hydrated 8-quinolinol chelates of Cu(II), Ni(II), Co(II), Cd(II), Zn(II), Mn(II) and Mg(II). Data presented are the heats of dehydration, kinetics of dehydration, and high temperature reflectance spectra of the hydrated and anhydrous compounds.

EXPERIMENTAL

Preparation of complexes

The 8-quinolinol (Eastman Organic Chemicals Co.) was used without further purification. All metal salts, solvents, and other materials were of reagent quality and were used without any further treatment. The general method of preparation was precipitation by ammonia solution from a buffered water–ethanol solution of 8-quinolinol and the appropriate metal salt. The precipitated complexes were collected on a Büchner filter, washed three times with distilled water, and then air-dried for 24 h at room temperature.

Analysis of complexes

Water content was determined by mass-loss on the thermobalance. 8-Quinolinol was determined by quantitative bromination of a 6 *M* hydrochloric acid solution of

TABLE I

ANALYTICAL DATA ON METAL CHELATES

Compound	*% Water*		*% 8-Quinolinol*	
	Found	*Theor.*	*Found*	*Theor.*
$Ni(Ox)_2 \cdot 2H_2O$	9.9	9.41	75.0	75.26
$Cu(Ox)_2 \cdot 2H_2O$	9.3	9.29	74.1	74.33
$Co(Ox)_2 \cdot 2H_2O$	9.8	9.40	75.0	75.22
$Cd(Ox)_2 \cdot 2H_2O$	7.9	8.25	65.7	66.01
$Mn(Ox)_2 \cdot 2H_2O$	10.8	9.50	75.7	76.01
$Mg(Ox)_2 \cdot 4H_2O$	19.7	18.74	73.8	74.94
$Zn(Ox)_2 \cdot 2H_2O$	9.1	9.25	73.7	73.98

the chelate with potassium bromate–bromide solution, the excess of bromide being determined iodometrically. The analytical data on the compounds are shown in Table I.

Instruments and technique

All thermogravimetric data were collected with a Dupont Model 950 Thermogravimetric Analyzer. A heating rate of 10° min^{-1} and a dynamic nitrogen atmosphere were used for all analyses. Sample sizes ranged in mass from 6 to 12 mg.

The calorimetry data were obtained with a Perkin-Elmer Model DSC-1B differential scanning calorimeter. The heating rate employed was 10° min^{-1} with sample sizes ranging in mass from 5 to 10 mg. The instrument was calibrated with an indium metal standard and the ratio of calories per arbitrary unit of chart area determined.

High-temperature reflectance spectra (h.t.r.s.) and dynamic reflectance spectra (d.r.s.) of the compounds were recorded on a Beckman Model DK-2A spectroreflectometer. A heated sample holder, as described by WENDLANDT AND DOSCH[10], was used. All spectra were scanned over 350–750 nm against a magnesium oxide reference. The heated sample holder was programmed with a Deltatherm (III) programmer; h.t.r.s. scans were made at intervals of 20° from ambient temperature to 200°; d.r.s. scans were programmed at 10° min^{-1} from ambient temperature to 200°. For d.r.s. curves, the wavelength chosen was that on the h.t.r.s. curve which showed the greatest change with temperature.

RESULTS

Heats of dehydration

These are given in Table II.

Kinetics of dehydration

The activation energies, E_a, for the dehydration of the chelate hydrates were determined by the method proposed by BROIDO[11] from thermogravimetric data. This method is based upon the determination of the fraction of unreacted material, y, as a function of temperature, T. The value of $\ln \ln(1/y)$ is plotted as a function of $1/T$. As in the conventional Arrhenius plot, the slope of the line is proportional to the acti-

TABLE II

HEATS OF DEHYDRATION OF CHELATE HYDRATES

$M(Ox)_2 \cdot nH_2O$	ΔH(*kcal*)	
	Per mole of complex	*Per mole of* H_2O
$Ni(Ox)_2 \cdot 2H_2O$	32.6 ± 1.6	16.3 ± 0.8
$Cu(Ox)_2 \cdot 2H_2O$	23.1 ± 1.2	11.6 ± 0.5
$Co(Ox)_2 \cdot 2H_2O$	30.7 ± 1.5	15.4 ± 0.8
$Cd(Ox)_2 \cdot 2H_2O$	26.5 ± 1.3	13.2 ± 0.7
$Mn(Ox)_2 \cdot 2H_2O$	28.5 ± 1.4	14.3 ± 0.7
$Mg(Ox)_2 \cdot 4H_2O$	26.9 ± 1.4	6.7 ± 0.4
$Zn(Ox)_2 \cdot 2H_2O$	28.8 ± 1.5	14.4 ± 0.7

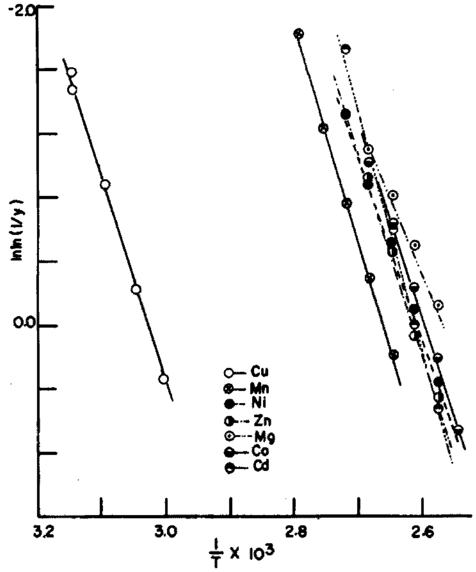

Fig. 1. Dehydration kinetics curves of chelate hydrates.

TABLE III

DEHYDRATION ACTIVATION ENERGIES OF CHELATE HYDRATES

Compound	E_a(*kcal mole*$^{-1}$)
$Ni(Ox)_2 \cdot 2H_2O$	29 ± 3
$Cu(Ox)_2 \cdot 2H_2O$	24 ± 2
$Co(Ox)_2 \cdot 2H_2O$	24 ± 2
$Cd(Ox)_2 \cdot 2H_2O$	30 ± 3
$Mn(Ox)_2 \cdot 2H_2O$	25 ± 3
$Mg(Ox)_2 \cdot 4H_2O$	16 ± 2
$Zn(Ox)_2 \cdot 2H_2O$	24 ± 2

vation energy, E_a. The activation energy is determined from the equation:

$$E_a = 0.960 \cdot R \cdot (\text{slope})$$

DRAPER[12] has developed a virtually identical method starting from purely thermodynamic considerations. The kinetics curves are shown in Fig. 1, while the activation energies are given in Table III.

H.t.r.s. and d.r.s. data

The h.t.r.s. and d.r.s. curves of $Mn(Ox)_2 \cdot 2H_2O$ are shown in Figs. 2 and 3, respectively. All of the other compounds were also studied by this technique but these data will not be reproduced here.

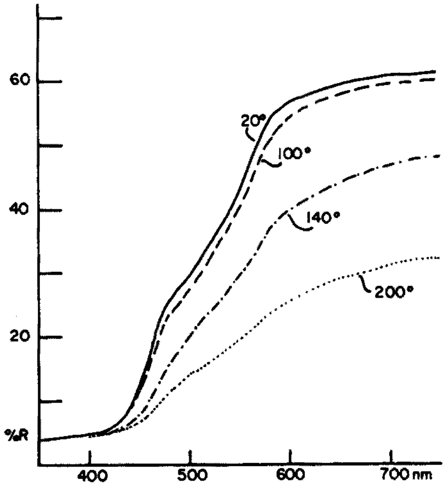

Fig. 2. H.t.r.s. curves of $Mn(Ox)_2 \cdot 2H_2O$.

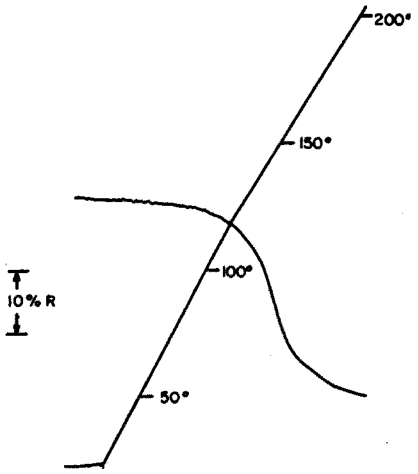

Fig. 3. D.r.s. curve of $Mn(Ox)_2 \cdot 2H_2O$; wavelength of 600 nm; heating rate of 5° min^{-1}.

DISCUSSION

The trend of the heats of dehydration can be correlated with general coordination theory. The low value in kcal $mole^{-1}$ of water for $Mg(Ox)_2 \cdot 2H_2O$ indicates a weak Mg–H_2O bond; since the magnesium(II) ion has no low-lying *d* orbitals, it is not expected that a coordinating ligand would be held too strongly. The main factor, then, in stabilizing the hydrated complex is probably crystal lattice energy rather than the strength of the coordinate bond. The water might more correctly be termed water of crystallization than water of coordination. The trend for the series of complexes Mn–Co–Ni–Cu–Zn, is in accord with crystal field theory. Manganese(II) and zinc(II) being, respectively, d^5 and d^{10}, have no crystal field stabilization energy contribution to the bonding; the strength of the metal–water bond in these complexes is determined by electrostatic effects and covalent bonding. The same argument applies to the stability of cadmium, another d^{10} ion. Cobalt(II) (d^7) and nickel(II) (d^8) show the trend that would be expected from the contribution of crystal field stabilization energy. The Jahn–Teller effect is a possible cause of the low heat of dehydration value for the copper(II) complex; the water molecules are relatively far away from the central metal ion, compared to the closely held 8-quinolinol groups, and are therefore bonded less strongly. The calorimetric data indicate that all the water molecules are equivalent. In every case, the dehydration is characterized by a single, continuous peak.

The kinetics data reinforce the inferences drawn from the trend of the heats of dehydration. The lower thermal stability of the copper(II) complex is apparent;

there is also the obvious difference in activation energies of all the other members of the series from that of $Mg(Ox)_2 \cdot 2H_2O$.

The magnesium(II) ion, even though it has no low-level *d* orbitals, forms a thermally more stable complex than does copper(II) because of the lattice energy. The higher charge/radius ratio of magnesium(II) and the distortion produced in copper(II) by the Jahn–Teller effect probably more than offsets the advantage of *d*-orbital availability in the latter. The markedly lower energy of activation for the magnesium complex argues that a different kind of bond is being broken than that in the complexes of the transition metals. In this complex, once the lattice has been opened by thermal agitation, less energy is required to remove the water than is required in the other complexes. In the other complexes, namely those of cobalt(II), nickel(II) and copper(II), the crystal field stabilization energy must be overcome; this would be expected to be greater than that of the water in the opened lattice of the magnesium(II) complex. In the complexes of manganese, zinc, and cadmium, even though there is no crystal field consideration, the increased electrostatic and covalent forces must be dealt with. The difference in activation energies then appears to be the difference in the type of water bonding: in the magnesium(II) complex, the water may be water of crystallization occupying lattice sites, and the water in the other complexes is actually water of coordination.

There does not appear to be a simple explanation for the change in reflectance upon dehydration. Depending upon the complex, the spectrum would be due to *d–d* transitions, charge transfer (ligand to metal), or both. In the complexes of manganese(II), cobalt(II), nickel(II) and copper(II), *d–d* transitions are to be expected; however, there is also the possibility of charge-transfer spectra. In the complexes of magnesium(II), zinc(II), and cadmium(II), where *d* electrons are absent, or else the *d* subshell is filled, charge-transfer spectra would seem to be most likely.

In the manganese(II), cobalt(II) and nickel(II) complexes, the decrease in reflectance could be accounted for by a change in coordination number. If it were assumed that the hydrated chelates were octahedral and went to a tetrahedral form on dehydration, then the decrease in reflectance could be justified in terms of reduced splitting between the *d* levels that occurs with the change in coordination number. Copper(II), however, does not exhibit this decrease in the red region; the change in reflectance is characterized by the disappearance of a band centered at 520 nm.

The magnesium(II) complex exhibits only a transitory change in reflectance. In the range 120–160°, the red region decreases in reflectance and a shoulder appears at 375–450 nm; however, at 200°, the red reflectance has returned to the original level and the original absorbance band has moved slightly from 470 to 500 nm. In the zinc(II) and cadmium(II) complexes, change in reflectance is characterized by movement to longer wavelengths of the absorption band at the blue end of the spectrum; virtually no decrease is observed in the red region. The beginning of the shoulder shifts, for the zinc(II) complex is from 500 to 575 nm, and, for cadmium(II), from 475 to 520 nm. The magnesium(II), cadmium(II) and zinc(II) ions are colorless; however, they do possess excitation bands in the near ultraviolet. The change in the position of this band upon dehydration may be due to the changing of the type of bonding; shifting of position and changes of band width are common occurrences when the type of coordination is changed. Changes in the reflectance spectrum appear to be associated with the type of structure. No determinations of the coordination number of structure of the chelates, in either the hydrated or anhydrous states have been made. Until the structures of the chelates have been determined, no definite assignments can be made.

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SUMMARY

The thermal dehydration of the 8-quinolinol chelate hydrates of Ni(II), Co(II), Cu(II), Cd(II), Mn(II), Mg(II), and Zn(II) was studied by thermogravimetry, differential scanning calorimetry, h.t.r.s. and d.r.s. Calorimetric data indicated that the heats of dehydration were correlatable with crystal field and electrostatic theory. The thermogravimetric data, applied in a different type of solid state kinetics equation, indicated that there was a difference in type of water bonding between that in the magnesium(II) complex and the other complexes. Changes in reflectance spectra upon dehydration were ascribed to possible changes in coordination for the complexes of Co(II), Cu(II), and Ni(II), involving the *d*-orbital splittings, and to changes in coordination affecting charge transfer in the complexes of Mg(II), Zn(II), and Cd(II).

RÉSUMÉ

Une étude est effectuée sur la déshydratation thermique des hydrates de chélates 8-quinolinol–Ni(II), Co(II), Cu(II), Cd(II), Mn(II), Mg(II) et Zn(II), par diverses méthodes. Les résultats calorimétriques indiquent que les chaleurs de déshydratation sont en corrélation avec la structure cristalline et la théorie électrostatique. Par thermogravimétrie, on observe une différence de type de liaison avec l'eau entre le complexe de magnésium et les autres complexes. Les spectres de réflectance indiquent des changements possibles dans la coordination des complexes de cobalt, de cuivre et de nickel et des changements dans la coordination affectant le transfert de charge dans les complexes du magnésium, du zinc et du cadmium.

ZUSAMMENFASSUNG

Es wurde die thermische Dehydratisierung der 8-Chinolinol-Chelathydrate von Ni(II), Co(II), Cu(II), Cd(II), Mn(II), Mg(II) und Zn(II) mittels thermogravimetrie d.s.c., h.t.r.s. und d.r.s. untersucht. Die kalorimetrischen Werte ergaben, dass die Dehydratisierungswärmen mit Kristallfeld- und elektrostatischer Theorie in Beziehung zu setzen waren. Die thermogravimetrische Ergebnisse, die in einer besonderen Gleichung für die Kinetik im festen Zustand angewendet wurden, zeigten einen Unterschied in der Art der Wasserbindung zwischen dem Magnesium(II)-Komplex und den anderen Komplexen. Änderungen der Reflexionsspektren bei Dehydratisierung wurden im Falle der Komplexe von Co(II), Cu(II) und Ni(II) einem möglichen Wechsel in der Koordination und Aufspaltung der *d*-Orbitale, im Falle der Komplexe von Mg(II), Zn(II) und Cd(II) Koordinationsänderungen mit Einwirkung auf den "Charge transfer" zugeschrieben.

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THE DETERMINATION OF TIN IN GEOLOGICAL MATERIALS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Tin is a trace element of great geological interest because it is often used as a geochemical indicator, but its determination in rocks at Clark level concentrations is not easy. In igneous rocks, the mean concentration varies between 30 and 40 p.p.m.[1], but in some minerals, *e.g.* muscovite, biotite, amphibole, the values may be about ten times higher. Much less is known about tin in sulphide minerals where its concentration may vary from less than 1 p.p.m. up to thousands of p.p.m. Atomic absorption spectroscopy could provide a sound method of solving this analytical problem, but only relatively high concentrations of tin in rocks have so far been determined, mainly in connection with mining activities[2,3].

It is now well established that the highest sensitivity for tin is found in air–hydrogen flames, in which interferences are more likely to occur owing to the relatively low temperature. The problems of determining tin at low concentrations therefore involve attaining a low detection limit and simultaneously eliminating interferences.

The sensitivity (p.p.m. for 1% absorption) reported in the literature is 1.2 p.p.m. in an air–hydrogen flame[4]. With a long absorption path device and an oxygen–hydrogen flame, AGAZZI found 0.025 p.p.m.[5]. In the present work, the long absorption tube method described previously[6] was applied, and interferences arising from ores and minerals were thoroughly investigated.

EXPERIMENTAL

Most measurements were performed with the equipment described earlier[6], which consisted of a Zeiss SPM 1 monochromator with a d.c. measuring device, and a long tube into which a flame from a direct injection burner was directed. Opaque silica tubes, 45 cm long with an inner diameter of 13 mm, were used; the tube was heated in an electric furnace.

Measurements with air–acetylene and nitrous oxide–acetylene flames were done with a Techtron AA4 Atomic Absorption Spectrometer. In all cases an ASL tin hollow-cathode lamp was used.

The standard stock solution of tin was prepared by dissolving 1 g of pure tin metal in 10 ml of concentrated hydrochloric acid at a temperature not exceeding 50°. The solution was then transferred to a 1-l volumetric flask and diluted to the mark.

Tin solution without chloride ions was prepared by dissolving 0.1 g of tin metal in 5 ml of 1+1 nitric acid directly in a 50-ml volumetric flask with constant cooling; this solution must be kept at low temperature and prepared daily.

RESULTS

Analytical lines of tin

Table I shows the relative sensitivity values for the three most sensitive tin lines reported by different authors for different flames; the sensitivity reported for the Sn 2246-Å line is always considered as 1. From this Table it is obvious that the lower the temperature of the flame, the poorer is the sensitivity of the line Sn 2355 Å compared to Sn 2246 Å. For the Sn 2355-Å line this is understandable because the population of its lower level $5p^2\ ^3P_1$ with an energy of 1692 K decreases correspondingly[7].

TABLE I

RELATIVE SENSITIVITIES FOR SOME TIN LINES IN DIFFERENT FLAMES

Flame	*Wavelength (Å)*			*Reference*
	2246	*2863*	*2355*	
C_2H_2–N_2O	1	1	0.8	
C_2H_2–air	1	1	1	4
H_2–air	1	1	1.5	
C_2H_2–N_2O	1	1.8	1.3	
C_2H_2–air	1	1.8	1.4	7
H_2–air	1	1.6	2.0	
C_2H_2–N_2O	1	1.3	0.74	
C_2H_2–air	1	1.4	1.2	
H_2–air	1	1.2	1.4	
H_2–air in heated tube	1	2.6	3.6	This work
H_2–air in unheated tube	1	3.6	5	

The longitudinal distribution of tin atoms

For this measurement a tube made from optical quartz with an inner diameter of 11 mm was used and the absorption was measured perpendicularly to the tube axis; of course, no electric furnace was employed. A direct injection burner with a stainless steel orifice was directly fitted to the entrance of the tube so that no ambient air was entrained into the tube. The results (Fig. 1) confirm previous observations[8] that maximum sensitivity is reached when the hydrogen flow is considerably greater than the air flow but that a further increase in the hydrogen flow beyond this maximum causes a decrease in sensitivity.

The situation may, however, be changed if some interfering elements are present. In Fig. 2, the effect of the hydrogen flow on the absorbance of tin in presence of hydrochloric acid and chromium are given; these measurements were done under normal working conditions, *i.e.* measuring the absorbance along the tube axis. It can be seen that in presence of chromium the absorbance does not decrease with increasing hydrogen flow.

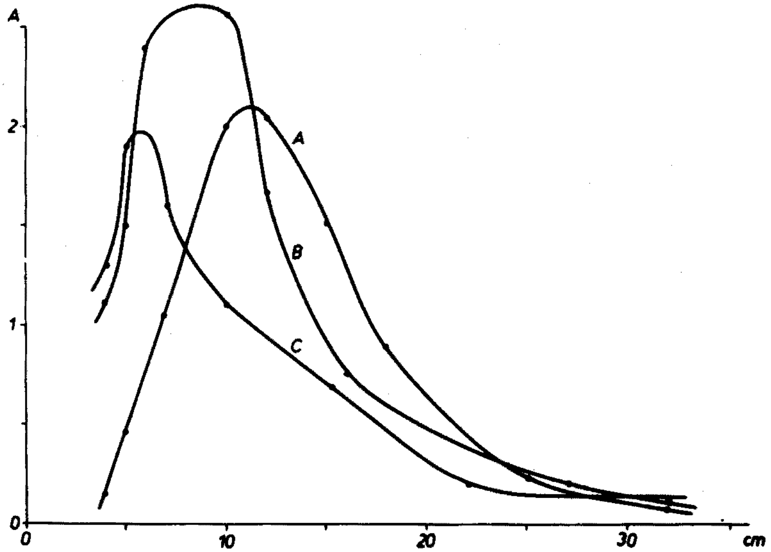

Fig. 1. Longitudinal absorption profile of tin in the tube. A solution of 200 p.p.m. of tin in 0.5 M hydrochloric acid was aspirated. The horizontal axis shows the distance from the entrance end of the tube. The air flow rate was constant (2 l min^{-1}). (A) Hydrogen flow rate 4.2 l min^{-1}; (B) hydrogen flow rate 10 l min^{-1}; (C) hydrogen flow rate 14.5 l min^{-1}.

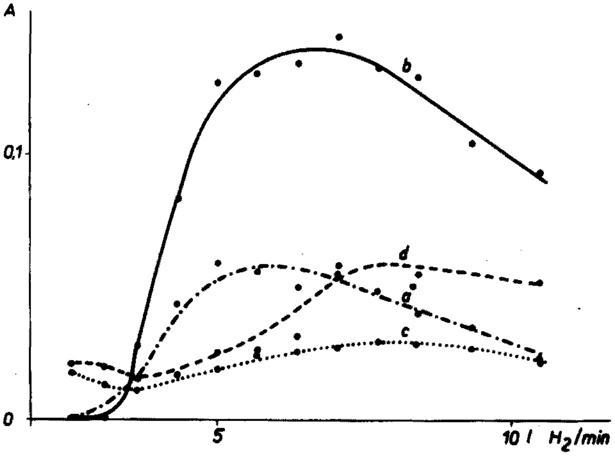

Fig. 2. Absorbance of tin with various hydrogen flow rates at a constant air flow of 2.5 l min^{-1}. Each solution contained 2 p.p.m. of tin. (a) Pure aqueous solution; (b) 1.5 M hydrochloric acid; (c) 300 p.p.m. chromium(III) in water; (d) 300 p.p.m. chromium(III) in 1.5 M hydrochloric acid.

The effect of anions

In common flames, the effect of anions on tin absorbance is only slight. With the Techtron AA4 spectrophotometer and an air–hydrogen flame it was found that a hundred-fold amount of sulphuric acid lowered the absorbance by about 15%. The readings in 1.5 M nitric acid and hydrochloric acid were identical. However, with the long tube device, acids had a marked influence (Fig. 3). All the measurements were performed at the hydrogen flow corresponding to maximum sensitivity, *i.e.*

about 7 l min^{-1}. At lower hydrogen flows, the depressive effect of nitric acid diminished and at a hydrogen flow of about 3 l min^{-1}, nitric acid had even a slight enhancing effect.

The effect of cations

The effects of various cations were studied and many were found to interfere. For these measurements, it was again important to set the hydrogen flow for maximum sensitivity for the pure tin solution, because some elements, especially iron,chromium, molybdenum and manganese, shifted the maximum on the absorbance–hydrogen

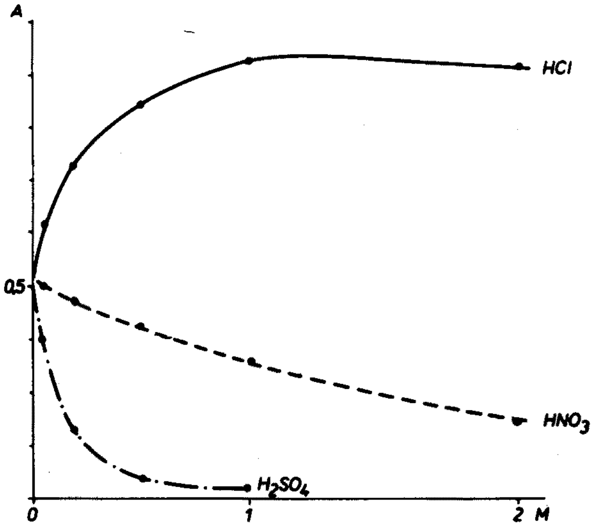

Fig. 3. Absorbance of tin in various acidic media. Each solution contained 2 p.p.m. of tin.

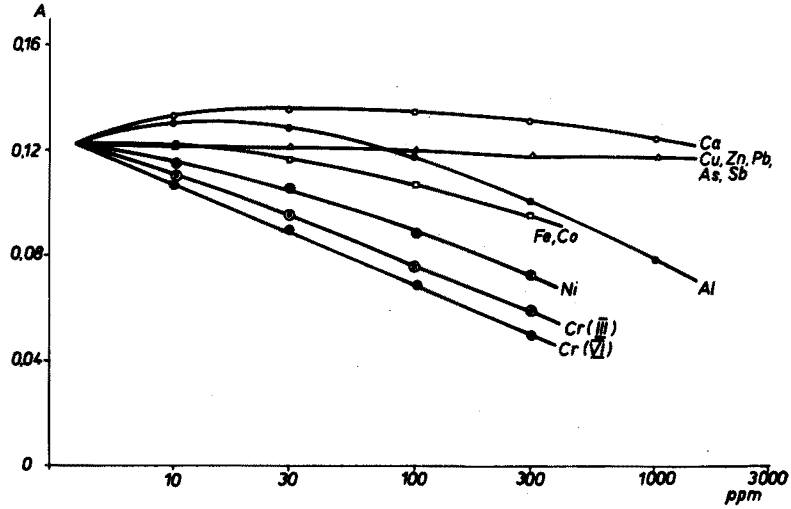

Fig. 4. Interferences of cations on tin. Each solution contained 2 p.p.m. of tin in 0.6 *M* hydrochloric acid.

flow curves towards higher hydrogen flows. However, when this slightly higher hydrogen flow was used initially, enhancement of tin absorption was still observed after addition of these elements. The results are shown in Fig. 4 and summarized in Table II. These interferences are basically the same at different hydrochloric and nitric acid levels, but for some elements of the iron group (Fe, Co, Ni, Cr, Mn) they are somewhat lower in nitric acid solutions.

TABLE II

CATIONIC INTERFERENCES IN 0.5 *M* HYDROCHLORIC ACID

Interfering element	*% Error for 2 p.p.m. Sn in presence of*	
	30 p.p.m.	*300 p.p.m.*
Na	20	−16
K	2	−6
Cu(II)	2	−5
Ca	12	8
Zn	2	−5
Al	8	−16
Pb(II)	2	−5
As(III)	2	−5
Sb(V)	2	−5
Cr(III)	−20	−50
Cr(VI)	−25	−60
Mo(VI)	−8	−30
Mn(VII)	2	−6
Fe(III)	−4	−20
Co	−4	−20
Ni	−12	−40

For iron and some other cations with a strong depressive influence, a "memory effect" of the interference was observed; this could amount to 50% of the original value. It seems that iron is deposited on the walls of the tube and is later released in quantities sufficient to affect the reactions by which tin is atomized.

To avoid all memory effects including those for tin itself, it is advisable to clean the tube frequently by spraying 6 *M* hydrochloric acid.

Background absorption was controlled by measuring the non-absorbing lines, Sn 2286 Å and Sn 2850 Å, for the two analytical lines tried Sn 2246 Å and 2863 Å, respectively, and was found to be basically the same. With the exception of lead and zinc, all other elements caused some background absorption. At 1000-p.p.m. levels, all the cations tested as well as sulphates and phosphates had a background absorbance between 0.01 and 0.02. Notable exceptions were sodium, calcium and aluminum which gave readings of 0.120, 0.027 and 0.078, respectively.

Mechanism of the interferences

Although it is not possible to explain the observed interferences fully, it may be useful to discuss them briefly, in the hope of contributing to the future solution of the "tin mystery"[9]. Although long-path absorption tubes were used, the basic interferences should be similar to those in a free-burning air–hydrogen flame and a comparison with the results of other authors appears valid.

In the long-path absorption tube, hydrochloric acid had a strong enhancing effect whereas in a normal air–hydrogen flame no such effect appears to have been found[4,10]; however, in the earlier work, the reference solutions already contained a certain amount of hydrochloric acid, and the effect is probably due to an increased volatilization rate of tin chloride compared with tin(IV) oxide (b.p. 623° and 1425°, respectively) possibly combined with an easier atomization of SnCl than SnO.

The depressive effect of sulphuric acid is most probably a solute volatilization interference since it is independent of the flame gas composition.

Among the cations tested, Fe, Co, Ni, Cr, Mn and Mo constitute a special group; all of these had a depressive effect with a more or less strong memory effect, indicating that a true vapour phase interference was involved. It has been already suggested that the presence of hydrogen and hydroxyl radicals above equilibrium values plays an important part of the atomization efficiency in a long-path absorption tube with an air–hydrogen flame[8]. It is perhaps significant that nickel and chromium, which have the highest depressive effect are also effective hydrogenation catalysts and it seems plausible that this is so because they speed up attainment of the equilibrium concentration of these radicals. However, in a free-burning flame, JULIANO AND HARRISON[10] found an enhancement effect of cobalt on tin at different heights in the flame and different hydrogen flows. This is hardly compatible with the above explanation, unless the discrepancy can be explained by the considerably lower concentration of water introduced into the flame in their experimental arrangement.

For elements forming refractory oxides, an enhancing effect was found, in agreement with JULIANO AND HARRISON[10]. This enhancement started at relatively low concentrations of the interfering ion, and it is quite likely that the mechanism involved includes some reactions in the solid state before vaporization of the clotlets.

Elimination of interferences

Because of these complicated interferences and the lack of any simple method of overcoming them, the composition of the sample solutions must be strictly controlled or an addition method must be used for evaluation.

For the analysis of sulphide minerals, which can be decomposed without excessive amounts of additives and which should contain only a limited number of interfering elements, mainly iron, the addition method after decomposition with hydrochloric acid only was studied. The samples were digested by concentrated hydrochloric acid on a slightly warm sand bath. To eliminate losses of tin as the volatile tin(IV) chloride, 2 ml of 5% potassium chlorate were added to form potassium hexachlorostannate(IV). After decomposition, the volume of the samples was adjusted with azeotropic hydrochloric acid and the solutions were directly measured. The results were reproducible but were 30–40% lower compared with polarographic determinations. Samples of galena were used, and it was established that the precipitate of lead chloride formed during the decomposition did not occlude any tin. However, when the undissolved residue was decomposed by fusion with potassium fluoride and boric acid and added to the main portion, the results were in agreement; evidently, tin was also present as minerals, probably cassiterite, insoluble in acid. Nevertheless, owing to the variable content of iron and other interfering elements, the evaluation had to be done by an addition method and the results for galenites had very poor precision and accuracy.

For tin ores, BOWMAN[3] recommends decomposition by sintering with ammonium iodide, exploiting the volatility of tin iodide. This procedure was found unsuitable for tin contents below 0.1% mainly because of the high background absorption of ammonium iodide.

The commonly used decomposition by fusion with sodium peroxide and a subsequent separation of tin by electrolysis was therefore examined. None of the elements of the first electroanalytical group present in the samples interfere in the final determination, and with the exception of antimony, copper and lead, are present only in concentrations commensurable with tin. Arsenic is reduced on the cathode to arsine and volatilizes.

At very low concentrations tin is not completely deposited on the cathode because it forms tin(IV) complexes which are difficult to reduce. Sand[11] recommended electrolysis in the presence of hydroxylamine, hydrochloric acid and copper(II), but it was found that for a complete electrolytic deposition, lead was also necessary (Table III). When the melt of sulphide minerals is dissolved with sodium peroxide in water, tin dissolves as sodium stannate, antimony(V) is precipitated as $Na_2H_2Sb_2O_7 \cdot 8\,H_2O$, lead partly forms a plumbate and partly precipitates as PbO_2. This is favorable for the electrolysis because at high lead contents the electrodeposit does not stick properly to the cathode.

TABLE III

THE INFLUENCE OF LEAD AND COPPER ON THE ELECTRODEPOSITION OF TIN

(500 μg of tin was taken and the cathode was coated with copper, except where specified otherwise. All solutions contained 5 ml of concentrated hydrochloric acid and 5 ml of 10% hydroxylammonium chloride in 100 ml)

Cu added (mg)	*Pb added (mg)*	*Sn found (%)*	*Cu added (mg)*	*Pb added (mg)*	*Sn found (%)*
5	0	0	0.5	15	102.4
5	0.1	94	1	15	102.8
5	0.3	90	3	15	100.4
5	0.5	96	5	15	100.6
5	1	102	0	15	76[a]
5	3	102	0	15	80[a]
5	15	101.2	0	0	0
0	15	102	5	15	90[b]
0.1	15	99.6	5	15	115[b]
0.3	15	100.4			

[a] The cathode was not coated with copper.
[b] Only 5 μg of tin was taken.

RECOMMENDED PROCEDURE

Sulphide minerals

Thoroughly mix 1 g of the sample with 10 g of sodium peroxide in a sintered corundum crucible. For sulphoantimonates containing more sulphur, increase the amount of peroxide to 15 g. Cover the crucible with a lid and heat slowly with a small flame. When part of the peroxide has fused, increase the heating to reach 500–600° (dark red glow). After 5–10 min, allow the melt to cool; transfer the crucible to a 250-ml beaker and extract with 150 ml of water. Rinse and remove the crucible, add 1 g of sodium peroxide to the extract and boil briefly. Cool the solution, transfer it to a 250-ml volumetric flask and dilute to the mark with distilled water. When the precipitate has settled, pipette a clear aliquot of 50–100 ml into a 250-ml beaker, neutralize with 1+1 hydrochloric acid, and add 20 ml more of this acid followed by 10 ml of 10% hydroxylammonium chloride solution and 1 ml of 2% copper sulphate pentahydrate solution (5 mg Cu). If the samples do not contain lead, add 10 ml of 0.2% lead chloride solution (15 mg Pb).

Adjust the volume to *ca.* 200 ml and electrolyze with Fisher net electrodes, the cathode being covered with 5 mg of copper, at 60–80°, with 1.5–2 V and a current of 0.7–1 A for 20–25 min. Rinse the electrodes with water without switching off the current. Dissolve the deposited metals from the cathode in a 150-ml beaker with 10 ml of cold concentrated hydrochloric acid, and dilute the solution to 50 ml in a volumetric flask.

Silicate rocks

Follow the procedure given above but use a larger sample (up to 3 g); the excess of sodium peroxide need not be so high and before electrolysis lead is always added.

Measurement procedure. Switch the furnace with the absorption tube on about 1 h, and the tin lamp about 30 min, before use. Set the wavelength to 2246.05 Å, the entry and exit slit to 23 μm, and the air pressure to 1 atm. Adjust the hydrogen pressure to give maximal tin absorption when spraying a standard. Use standard solutions over the range 0.1–2 p.p.m. containing the same amount of hydrochloric acid as the samples.

Between every two samples, spray water and from time to time, but always after samples with high tin contents, clean the tube by spraying 6 *M* hydrochloric acid. The solutions have no background absorption.

TABLE IV

DETERMINATION OF TIN IN GEOLOGICAL SAMPLES

Sample	*Sn found (%)*	
	Atomic absorption	*Other method*
Spilite ZGI	0.00023	0.00025[a]
Granite ZGI	0.00045	0.0005[a]
Shale ZGI	0.00045	0.0005[a]
Greisen.granite-280/64	0.084	0.09[b]
Greisen.granite-281/64	0.17	0.17[b]
Greisen.granite-282/64	0.26	0.26[b]
Greisen.granite-283/64	0.40	0.42[b]
Greisen.granite-486/63	0.023	0.028[b]
Greisen.granite-487/63	0.059	0.06[b]
Greisen.granite-491/63	0.0094[c]	0.010[b]
Sfalerite 975/65	0.075	0.073[d]
Galenite I 2108/62	0.031	0.033[d]
Galenite II 527/63	0.041[e]	0.045[d]
Greisene I	0.16	0.16[b]
Greisene II	0.23	0.23[b]

[a] Recommended values ZGI[18].
[b] Polarography.
[c] Average from 8 determinations.
[d] Average from 6 determinations by oscillopolarography after silica gel separation.
[e] Average from 20 determinations.

Precision and accuracy

With 3 g of sample, the lowest concentration which can be determined is 2 p.p.m. The precision expressed as the relative deviation calculated from 17 repeated analyses of one galena sample was 5.45%.

The accuracy was checked on some reference standard materials as well as on samples analysed by polarography after separation of tin on a silica gel column[12]. All the results were found to be in good agreement (Table IV).

SUMMARY

Tin can be determined in geological samples by atomic absorption spectroscopy by using a 45-cm long-heated absorption tube. After decomposition by fusion and electrodeposition separation, the method is sufficiently accurate and precise down to 2 p.p.m. of tin in silicate or sulphide samples. The behaviour of tin in the absorption tube, and cationic and anionic interferences were studied.

RÉSUMÉ

L'étain peut être dosé dans des échantillons géologiques, par spectroscopie par absorption atomique, en utilisant un tube d'absorption chauffé, de 45 cm de longueur. Après décomposition par fusion et séparation, par électrodéposition, la méthode est suffisamment précise et exacte, jusqu'à 2 p.p.m. d'étain dans un silicate ou un sulfure. On examine le comportement de l'étain dans le tube d'absorption, ainsi que les interférences cationiques et anioniques.

ZUSAMMENFASSUNG

Zinn in geologischen Proben kann durch Atomabsorptionsspektroskopie unter Anwendung eines 45 cm langen erhitzten Absorptionsrohrs bestimmt werden. Nach Schmelzaufschluss und elektrochemischer Abscheidung ist die Methode bis zu 2 p.p.m. Zinn in Silicat- oder Sulfidproben genügend genau. Das Verhalten von Zinn im Absorptionsrohr sowie kationische und anionische Störungen wurden untersucht.

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A FLAME EMISSION TECHNIQUE FOR OBTAINING STRUCTURAL INFORMATION FROM ORGANIC MOLECULES

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(Received March 9th, 1970)

The use of organic emission spectra for qualitative analysis has recently been investigated. Preliminary studies made use of certain combustion product molecules for gas chromatography determinations. A flame emission detector of this type was first described by GRANT[1]. The detector was based on the increase in the total emission signal of a hydrogen–air flame, but no wavelength selectivity was attempted. Response was linear with sample weight. GRANT also confirmed that C_2 and CH radiation from air–hydrogen and oxy–hydrogen flames is stronger for aromatics or unsaturates than for saturates. More recently, JUVET AND DURBIN[2] reported on the detection of metal halides and metal chelates, and the CH and C_2 molecules relative emission from organic compounds. BRAMAN[3], using an air–hydrogen flame emission detector in conjunction with a gas chromatograph, studied the influence of structure on response ratios of CH to C_2 emission for some organic compounds and was able to identify certain heteroatom compounds in a chlorinated methane series, an aromatic series, and a three-carbon series of heteroatom compounds. From the influence of structure on response ratios, BRAMAN demonstrated the potential use of the dual flame ionization–flame emission detector in qualitative identification of peaks. MCCREA AND LIGHT[4] used limited-area flame spectroscopy to study the prominent band heads of the CH and C_2 species. They found that the emission intensity of the CH and C_2 species is a quantitative estimate of the concentration of the parent molecules, and that the analytical curves for hydrocarbons in methanol are linear over the concentration range utilized. BUELL[5] used a similar method to study spectral emissions from combusting organic solvents and found that as excitation potentials for molecules increased, the height of maximum emission in the flame decreased. ROBINSON AND SMITH[6] investigated the emission spectra of organic liquids in an oxy–hydrogen flame and suggested that qualitative analysis of organic compounds may be feasible by this process. PARSONS[7] used an air–hydrogen flame and found that the technique can be used to distinguish between geometrical isomers of alcohols thereby confirming ROBINSON's suggestion.

In the present paper, data for amines and alcohols are compared and it is shown that one can differentiate geometrical isomers as well as compounds of greater structural differences. It will also be shown that the trends observed by PARSONS[7] are valid for the amines and other organic compounds. The measurements made in

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this investigation are based on the fact that the emission intensity of certain molecular fragments, *e.g.*, the CH, C_2, CN and NH molecules, produced from the combustion of organic species in the flame are directly proportional to the number of these molecules existing per unit volume in the hot flame gases. The number of these molecules is a function of the bonding energy of the parent molecule, a function of the number of corresponding atoms in the parent molecule, and a function of the collisional processes occurring in the flame. Thus, the intensity measurements of several molecules can be used to determine differences between similar compounds.

EXPERIMENTAL

Apparatus

A simple flame photometer set-up (see Fig. 1) was used for this investigation. The optics consisted of a 0.25-m Jarrell Ash monochromator (Model No. 26-780) with an R.C.A. IP28 photomultiplier tube. The optical arrangement produced a resolution of about 0.8 nm. An air–hydrogen flame was produced by introducing hydrogen gas into the oxygen port of a medium-bore, total-consumption burner (Beckman, Model No. 4020). The burner was positioned such that the nozzle tip was level with the bottom of the monochromator slit. The fuel flow rate was con-

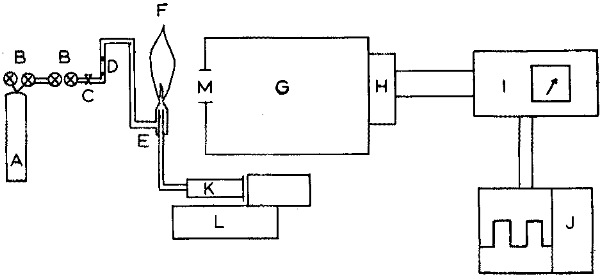


Fig. 1. Schematic diagram of experimental apparatus. (A) H_2; (B) regulators; (C) needle valve; (D) rotameter; (E) burner; (F) flame; (G) monochromator (f/3.6); (H) phototube; (I) power supply/electrometer; (J) strip chart recorder; (K) syringe of sample solution; (L) variable speed pump; (M) slit height, 2 cm.

TABLE I

OPERATING CONDITIONS FOR ENTRAINED AIR–HYDROGEN FLAME EMISSION MEASUREMENTS

Parameter	*Value*
Hydrogen flow rate	3.0 l min^{-1}
Sample solution flow rate	0.5 ml min^{-1}
Monochromator slit width	0.25 mm
Monochromator slit height	2.0 cm
Photomultiplier tube voltage	600 V
Chart speed	1.0 in min^{-1}
D.c. electrometer settings (full scale)	$0.5 \cdot 10^{-7}$ to $0.5 \cdot 10^{-8}$ A
Wavelength setting (CH molecule)	431.6 nm
(C_2 molecule)	517.1 nm
(CN molecule)	388.8 nm
(NH molecule)	336.7 nm

trolled by a five-stage regulation system. The sample solutions were force-fed into the burner by means of 10-ml glass syringes which were controlled by a variable speed Sage pump (Model No. 255-1). The samples were injected through a 19-gauge needle into a polyethylene tube which connected the burner capillary to the syringe needle.

The output of the photomultiplier tube was measured by a d.c. electrometer (Jarrell Ash, Model No. 26-780) and displayed on a Varian strip-chart recorder (Model No. G-2000) with a Disc integrator (Model No. 244). The operating conditions for the system are given in Table I.

Preparation of samples

Only the highest grade alcohols and amines commercially available, either ACS Reagent or Baker grade, were used. No attempt at further purification of the alcohols was attempted. Almost all of the amines were purified just before use, because of the rapid oxidation that often occurs; they were distilled from potassium hydroxide in a nitrogen atmosphere. Only the middle fraction of the distillate was used in carrying out the experiments. The purified amines were stored under a nitrogen atmosphere in order to reduce oxidation. A gas chromatograph (Carle, Model No. 6500) was used to determine the purity of the distilled chemicals. It was found that all were at least 98% pure except for isopropylamine and isopentylamine which were about 97% pure. The samples were prepared in 10, 5 and 2 mole-% solutions in methanol (A.R. Grade). This was done so that equal numbers of molecules would be introduced into the flame per unit time. The solutions were prepared on a weight basis using a top-loading Sartorius balance that had an accuracy of ±0.001 g. The solutions were prepared with an accuracy of better than ±1.0% which is well within the limits of experimental error.

Solvents other than methanol could also be used. The only important requirements in choosing a solvent are that the solvent and its combustion products are not themselves excessive emitters at the desired wavelengths and that the combustion of the solvent does not adversely affect the production and excitation of C_2, CN and CH species originating from the samples. Other factors must also be considered in choosing a solvent. The solvent should be available in sufficiently pure grade and have a viscosity and vapor pressure similar to those of the samples.

Sampling

It was statistically determined[7] that the glass syringes used were matched within experimental error; therefore, a separate syringe was used for each sample during the run. The syringe and burner capillary tube were connected together by a polyethylene tube and a 19-gauge needle. A single needle was used in conjunction with all the syringes. The syringe was placed in the Sage pump which controlled the sample flow rate. This method produced a steady flow of sample regardless of density and viscosity.

Each solution was sampled for 2 min. Before and after every two sample solutions, a run was made with the blank solution methanol. This was done to correct for drift during the experiment and to provide intensity data from which the emission caused by methanol could be subtracted from the total emission. Several (4–10) intensity measurements were taken for each compound investigated.

Measurements

A spectrum (300–800 nm) was taken of the sample (see Figs. 2 and 3). The most intense CH, C_2, CN and NH peaks were established, to give the best data for evaluation (see Table I). The monochromator was then manually adjusted to each particular wavelength of interest. A run consisted of taking intensity measurements of several sample and methanol blank solutions at one of the desired wavelengths then manually adjusting the monochromator to the next desired wavelength and repeating the procedure. At each wavelength, the sensitivity was adjusted to give a useful signal. The readings were obtained by means of the readout of the Disc integrator by which the noise could be averaged out.

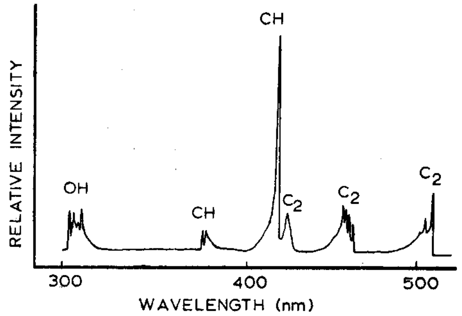


Fig. 2. Typical spectrum of an alcohol.

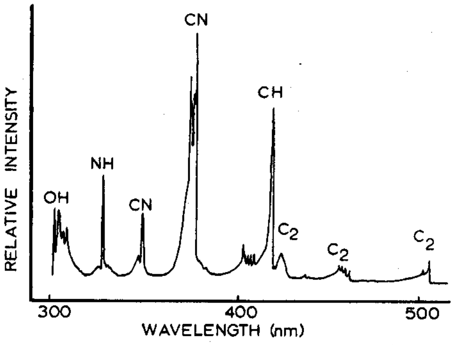


Fig. 3. Typical spectrum of an amine.

Reproducibility was affected by binding of the syringe plunger, which was therefore always tested for signs of binding before the start of a run, by rotating the plunger. If the plunger did not rotate freely, then the clamps holding the syringe were adjusted until the plunger rotated freely. For optimal reproducibility, it was best to let the flame burn for 15–20 min so that the characteristics of the burner were stabilized before measurements were made. Characteristics of a burner change whenever it is cleaned or dismantled, as well as slightly from day to day. Consequently, for best reproducibility the runs should be made on one day with the flame burning constantly. Reproducibility can also be affected by variations in room temperature, air pollutants, etc. As mentioned before, evaporation of the solution in the syringe was negligible. However, the solutions were not in the syringes for an appreciable length of time. If many solutions are being run at one time, new sample solutions should be put into the syringes every 60 min.

RESULTS AND DISCUSSION

Relative band intensities of the CH, C_2, and the CN band heads are shown in Table II. Measurements of the NH band head were also taken. However, the differences in the relative intensities were too small to give a pertinent evaluation of the compounds. At the wavelength of the CH band, a plot of relative emission intensity *versus* the carbon number was linear as shown in Figs. 4 and 5. The carbon number has little influence on the relative emission intensities of CN, whereas for the CH

TABLE II

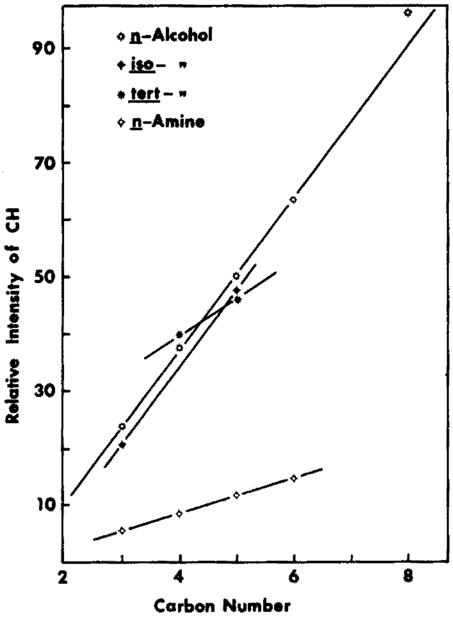
RELATIVE BAND INTENSITY ($\cdot 10^{-9}$ A)

Compound	*CH*	C_2	*CN*
Propylamine	5.5	2.8	6.7
Isopropylamine	4.2	2.3	8.0
Butylamine	8.4	3.8	6.4
Isobutylamine	8.7	4.6	6.6
Sec-butylamine	7.7	3.8	8.0
Tert-butylamine	7.3	4.5	9.1
Pentylamine	11.8	4.7	6.3
Isopentylamine	11.1	5.5	6.0
Tert-pentylamine	10.6	5.4	9.7
Hexylamine	14.8	6.0	6.5
Diethylamine	8.0	3.5	6.9
Dipropylamine	14.1	6.1	6.7
Diisopropylamine	12.4	6.3	9.5
Dibutylamine	17.9	7.8	6.0
Triethylamine	10.6	5.1	6.2
Propanol	23.8	32.8	
Butanol	37.8	32.4	
Pentanol	50.0	35.2	
Hexanol	63.3	34.7	
Octanol	96.0	34.7	
Isopropanol	20.6	41.2	
Isobutanol	38.7	38.5	
Isopentanol	48.8	38.5	
Tert-butanol	39.8	44.1	
Tert-pentanol	46.0	38.6	

and C_2 intensities, the carbon number appears to be one of the controlling factors of the intensity value. A plot of the relative emission intensity of the CH band *versus* the CN or C_2 bands also showed a similar linear response.

PARSONS[7] found a linear relationship with the alcohols, by plotting the relative intensities of CH *versus* C_2, that differed only in intercept for different homologous series. He also found that the compounds in each homologous series had the same slope within experimental error. In contrast, the amines (see Fig. 6) have different slopes for each homologous series. As can be seen in Fig. 4, the relative intensities of the alcohols are higher than those for the amines. The higher emission intensity measurements obtained for the alcohols may possibly be due to better burning characteristics, or possible nitrogen quenching, but no conclusive statements can be made.

BRAMAN[3], who investigated triethylamine at 388 nm with an air–hydrogen flame, observed higher sensitivity at the CH and C_2 wavelengths over that at the 388-nm CN band. He suggested that an air–hydrogen flame suppresses CN molecule



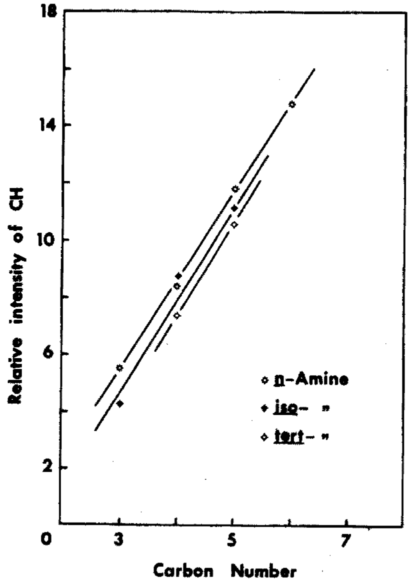


Fig. 4. Plot of CH intensity *versus* carbon number for various alcohols and amines.

Fig. 5. Plot of CH intensity *versus* carbon number for various amines.

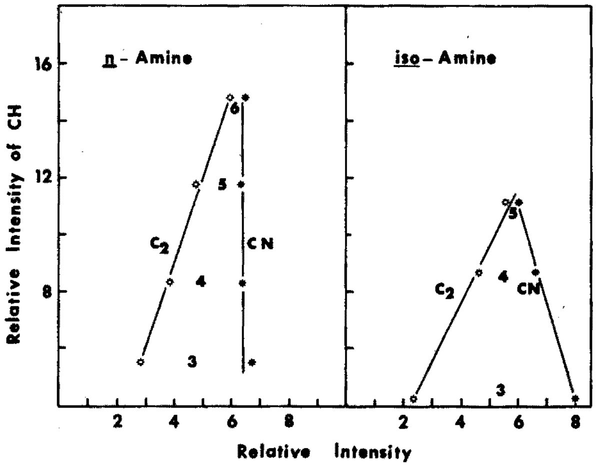


Fig. 6. Plot of CH intensity *versus* C_2 and CN intensity for *n*-amines and iso-amines.

formation or the subsequent excitation process. As can be seen in Table II, the CH and C_2 wavelengths are not always more sensitive than the CN wavelength.

The difference in intensities shown in Table II demonstrates the ability of the system to distinguish between the different samples. The CH and C_2 emission intensities appear to be generally proportional to the carbon number. The CN emission intensities appear to be generally inversely proportional to the carbon number. These trends can be explained by the availability of the carbon and nitrogen atoms in relation to one another. A trend similar to the CN emission intensity applies to the NH emission intensity. However, the slope for the NH emission was generally not as negative as the slope for the CH emission and varied little between homologous series. A comparison between *n*-propylamine and iso-propylamine indicates the variance of emission intensity on small structural changes. The differences in emission response for all the compounds examined, suggest that the qualitative identification of organic compounds appears to be possible by this technique.

An approximate empirical formula of the unknown compound can be determined by plotting the relative CH intensity *versus* % carbon, % nitrogen and % hydrogen. This can be done if it is known that there is an amine, alcohol, particular element, or functional group in the sample. Calibration curves for each individual instrument are necessary before the evaluation can be made; these can be made by running homologous series of the compounds desired. After the slopes for these are obtained, the data for the unknown sample can be evaluated.

Aromatic amines, mainly solids, were examined by the same procedures as for the saturated amines. After recrystallization, 2 mole-% solutions in methanol were made up. When aspirated, the solutions of solid aromatic amines tended to clog the burner very quickly, probably because of excessive evaporation of the solvent.

Another flame system was also used to relate the CH emission intensity of alkanes, alkylbenzenes, aldehydes and ketones to the C_2 emission intensity. Similar correlations were achieved from these observations. The apparatus was similar to that used to evaluate the amines and alcohols, except that various oxy–hydrogen flames were used with a Hetco burner (Model No. V-105). Pure samples were aspirated into the burner; this necessitated several corrections to achieve a molar response The results obtained by this method were less precise than those obtained by the method used to evaluate the amines and alcohols, because of flame temperature variations between the different compounds. The compounds with the higher carbon numbers were affected by self-absorption and temperature effects. However, the results showed a linear relationship between the intensity of the CH emission and the intensity of the C_2 emission. Similar results were obtained for both systems when aromatic compounds were examined, but insufficient compounds in each homologous series were examined to evaluate the data fully.

The method described here is by no means perfected. Difficulties caused by solutions of solids clogging the burner, could probably be avoided by using an oxy–hydrogen flame with the Hetco burner; the larger nozzle of the burner and the hotter flame produced should also give a more intense signal. Weaker solutions could have been used, but the intensity produced would have been very weak and hard to evaluate.

No attempt was made to optimize parameters. Reproducibility could be improved by optimizing the signal-to-noise ratio as suggested by PARSONS AND WINEFORDNER[8]. When the data for the saturated amines were normalized to the CH emission equalling 100, the relative standard deviations for the C_2 emission and the CN emission were 5.56% and 5.97%, respectively, based on 155 runs for all the compounds listed in Table II.

Qualitative identification of flame emission peaks of heteroatom containing compounds appears feasible by obtaining response intensities at different selected wavelengths and comparing them to known compounds at the same wavelengths. Other potential uses of flames emission studies are the study of the structure of organic compounds and the kinetics of the combustion of different compounds.

This research was supported in part by an A.S.U. Faculty Grant-in-Aid and by an ACS-PRF-Type G grant.

SUMMARY

The use of an entrained air–hydrogen flame to obtain structural information of amines and alcohols was studied. Differences in emission intensities of CH, C_2, and CN species indicate the possibility of qualitative analysis of organic compounds. A linear relationship was found to exist for members of different homologous series of amines and alcohols, when the intensity of CH emission was plotted *vs.* intensity of C_2 or CN emission.

RÉSUMÉ

Une étude est effectuée pour obtenir des informations sur la structure des amines et des alcools, par émission, avec une flamme air–hydrogène. Les différences d'intensités d'émission des particules CH, C_2 et CN indiquent la possibilité d'analyse qualitative de composés organiques.

ZUSAMMENFASSUNG

Die Möglichkeit, mit Hilfe einer Luft–Wasserstoff-Flamme Strukturinformationen von Aminen und Alkoholen zu erhalten, wurde untersucht. Unterschiede in den Emissionsintensitäten von CH, C_2 und CN ermöglichen eine qualitative Analyse organischer Verbindungen. Für die Glieder verschiedener homologer Reihen von Aminen und Alkoholen ergibt sich eine lineare Beziehung, wenn die Intensität der CH-Emission gegen die Intensität der C_2- oder CN-Emission aufgetragen wird.

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STUDIES OF THE CARBON CONTENT OF STEEL AND ITS DEPTH DISTRIBUTION BY MEANS OF PROTON ACTIVATION ANALYSIS

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The development of charged particle activation analysis of light elements in various materials has progressed rapidly during the past decade. With this technique, an element can be studied both on the surface and as regards its depth distribution below the surface[1].

Charged particle activation analysis carried out with ^{3}He-particles has been found to yield an extremely high degree of sensitivity[2]. The fluorine contamination on zircaloy surfaces and in various layers below the surface has successfully been studied[3] through the reaction $^{19}F(p,\alpha\gamma)^{16}O$. By means of (d,n) reactions combined with time of flight measurements it has been possible to determine carbon, nitrogen and oxygen on and under steel surfaces[4]. Oxygen concentrations at zirconium surfaces as well as the depth distribution of oxygen in the metal have successfully been determined[5] by spectroscopy with protons produced in the reaction $^{16}O(d,p)^{17}O$. This technique has found applications in studies of the diffusion mechanisms of oxygen in zirconium[6].

Carbon has previously been determined[7,8] in the surface of steel samples by means of the reaction $^{12}C(p,\gamma)^{13}N$; either the induced ^{13}N-activity or the prompt γ-radiation occurring at a proton energy of 0.46 MeV can be measured.

The cross-section curve for the reaction $^{12}C(p,\gamma)^{13}N$ exhibits resonances at proton energies of 0.46 MeV and 1.70 MeV, respectively[9]. At the 0.46-MeV resonance (total width $\Gamma = 35$ keV, cross-section $\sigma = 127$ mb), a γ-quantum of 2.36 MeV is emitted. At the 1.70-MeV resonance (total width $\Gamma = 70$ keV, cross-section $\sigma = 35$ mb), a γ-quantum of 3.51 MeV is emitted[9].

The aim of the present study was to extend the analysis to comprise both resonances in the carbon determination of steel. Since the accelerator used operates above 1 MeV, only the 1.70 MeV resonance could be utilized for surface studies, whereas both resonances could be considered in the depth distribution investigations.

At an appropriate proton energy, the carbon content both at the surface and in a layer below the surface of the material can be measured in a single operation utilizing both resonances.

In this study steel samples specially heat-treated in order to obtain carbon homogeneity were used for the depth distribution investigation. The aim was thus to demonstrate the degree of carbon homogeneity at various depths.

Straggling

In the depth distribution studies, the thickness of the layer investigated is somewhat different near the surface and in a layer deeper in the material. Close to the surface the layer thickness is about equal to the width of the resonance peak. Thus for the $^{12}C(p,\gamma)^{13}N$ reaction, the layer thickness relating to the 0.46-MeV resonance ($\Gamma=35$ keV) is ~ 0.25 μm, whereas the corresponding value for the 1.70 MeV peak ($\Gamma=70$ keV) amounts to ~ 1 μm. However, at depths farther from the surface the layer thickness relating to a selected proton energy becomes wider owing to proton straggling.

The mean square deviation of the energy loss, Ω_ε^2, for protons after passing a distance ΔR in the energy interval considered, is given by the following formula[10]:

$$\Omega_\varepsilon^2 = 4\pi Z_1^2 \cdot Z_2 \varepsilon^4 N \Delta R \qquad (1)$$

where Z_1 denotes the charge number of the incident particle and Z_2 is the number of electrons in the stopping atom; ε expresses the electronic charge and N is the number of atoms per volume unit.

The depth resolution, D_r, of the layer investigated is given approximately by the following expression:

$$D_r^2 \approx \Gamma^2 + (2\Omega_\varepsilon)^2 \qquad (2)$$

where D_r and Γ refer to full width whereas Ω_ε represents the half-width at half maximum height of the gaussian distributions considered.

From eqn. (2) the depth resolution is obtained in energy units. With known stopping-power parameters, D_r can be transformed to length units. Values of D_r for various depths in iron relating to the reaction $^{12}C(p,\gamma)^{13}N$ have been calculated.

EXPERIMENTAL

Radiation source and measurements

A proton beam from the 5.5-MeV Van de Graaff accelerator at Studsvik was used. The energy of the proton beam was varied between 1 and 4.5 MeV. The beam passed through a slit system, giving a homogeneous beam with a diameter of about 2 mm at the target.

A liquid nitrogen-cooled copper tube, coaxial with the beam, was introduced in the proton flight path for reducing the build-up of contaminants on the target. In order to simplify the current measurement the last part of the beam tube was insulated from earth. The charge collected at the target was measured with a current integrator. The current was within the range 1–10 μA throughout the experiment.

To detect the γ-rays a 3 × 3″ NaI(Tl) crystal was used, placed with its axis at 90° to the proton beam direction at distances between 70–150 mm from the target. Lead shielding was employed to protect the detector from backfround radiation. Output pulses from the detector were amplified and transmitted to a 400-channel pulse-height analyzer.

A 17-cm^3 germanium semiconductor detector was also used in the measurements.

The geometrical arrangement of beamline, target and detector is given in Fig. 1 (see also ref. 3).

Samples

Steel samples containing 0.07, 0.46 and 1.07% carbon (Sandviken Jernverk

AB) were studied. These samples had been submitted to special heat treatment at about 1100° in order to obtain carbon homogeneity. The homogeneity was tested by means of microscopic studies[11]. The samples were ground and mechanically polished before being irradiated with protons.

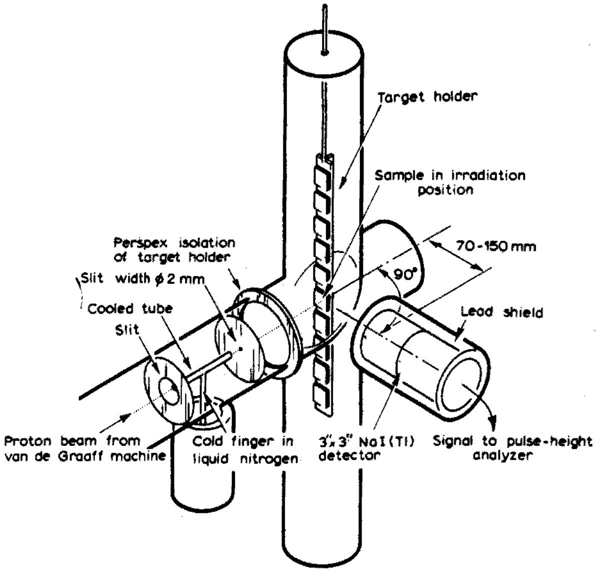
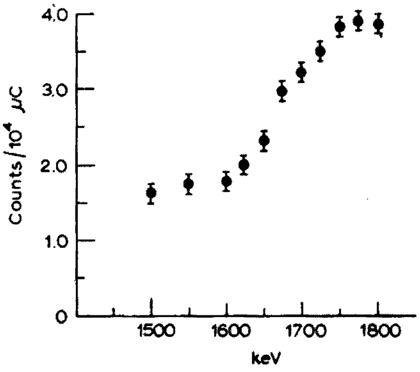


Fig. 1. Irradiation and measurement arrangement.



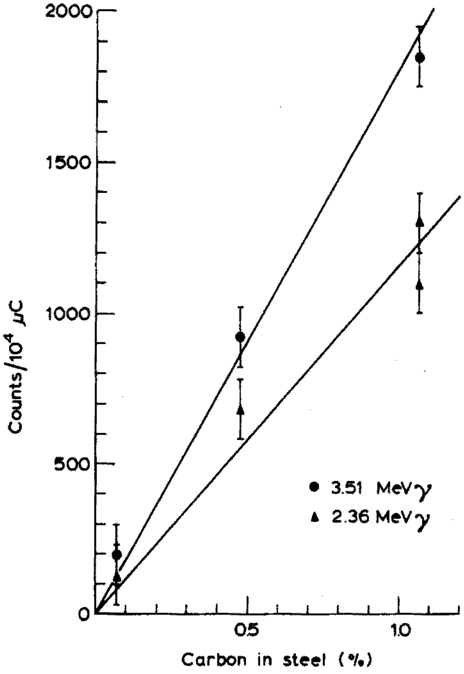
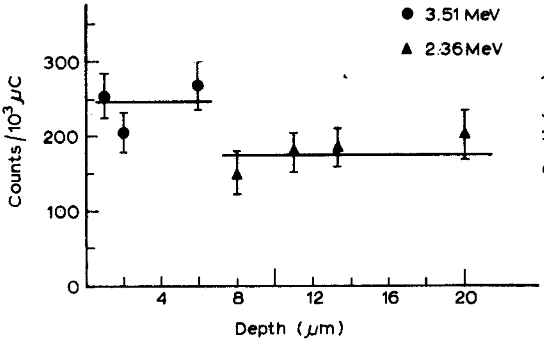


Fig. 2. Differential cross-section curve for the reaction $^{12}C(p,\gamma)^{13}N$ in a thick target of carbon.
Fig. 3. Proportionality of activities for different steel samples.

RESULTS

The differential cross-section curve for the reaction $^{12}C(p,\gamma)^{13}N$ applied in a thick target, revealing a resonance at the energy level 1.70 MeV[9], is given in Fig. 2. (The resonance at 0.46 MeV could not be investigated since the machine only functioned above 1 MeV.)



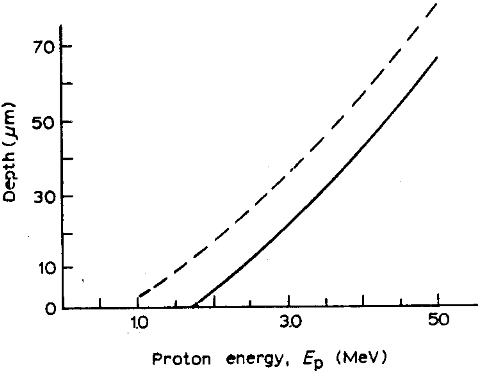
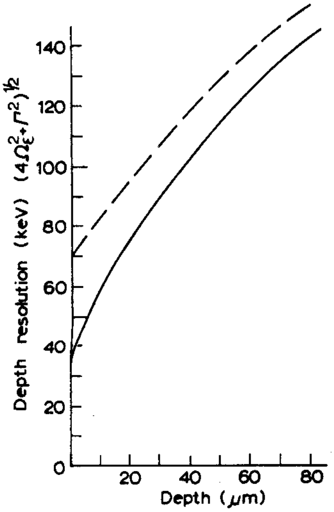


Fig. 4. Induced activity as a function of depth in iron (1.06% C).

Fig. 5. Calculated depths[12] in iron corresponding to proton energies. (E_p — 0.46) MeV (—) or (E_p — 1.70) MeV (---).



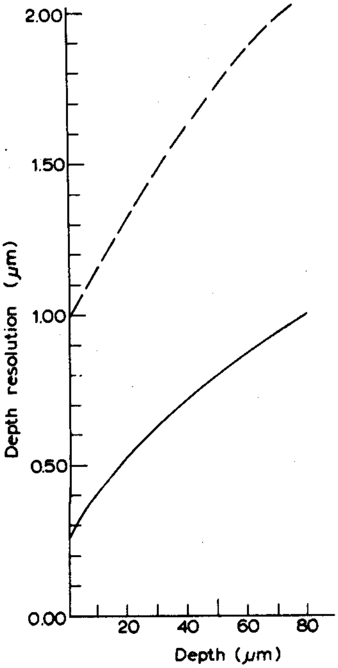


Fig. 6. Calculated depth resolution (keV) in iron as a function of depth[10]. (—) $\Gamma = 35$ keV (0.46 MeV resonance), (---) $\Gamma = 70$ keV (1.70 MeV resonance).

Fig. 7. Calculated depth resolution (μm) in iron as a function of depth[12]. (—) $\Gamma = 35$ keV (0.46 MeV resonance), (---) $\Gamma = 70$ keV (1.70 MeV resonance).

Figure 3 shows the proportionality of the activities observed for the steel samples containing 0.07, 0.46 and 1.06% carbon, both in the surface (3.51-MeV γ-radiation) and in a layer below the surface (2.36-MeV γ-radiation). In one of these samples (containing 1.06% carbon), the homogeneity of the carbon content in various layers was investigated by altering the proton energy (Fig. 4). Figure 5 gives the depth of the analyzed layer from the surface as a function of the proton energy. (Range-energy parameters are taken from ref. 12.) Figures 6 and 7 show the depth resolution of the layer studied in energy and length units, respectively, as a function of the depth from the surface. (These were calculated by means of formulae (1) and (2).)

DISCUSSION

The present study indicates that direct measurements of the prompt γ-radiation arising from the $^{12}C(p,\gamma)^{13}N$ reaction are limited to about 0.1% carbon in steel samples. At this carbon concentration several hours of measurement were needed in order to obtain a small peak in the high background induced in the steel samples (measured with a NaI(Tl) crystal). A germanium semiconductor detector did not yield any improvement in the results. On the other hand, analysis of the induced ^{13}N-activity by means of measurements of the annihilation radiation, showed an increased sensitivity, as previously reported[7,8]. The application of this technique to depth distribution studies is now in progress.

With increasing proton energy (above *ca.* 2.5 MeV) the background in the steel samples was observed to increase greatly, which limits the sensitivity of the carbon determination at greater depths.

The main advantage of using the reaction $^{12}C(p,\gamma)^{13}N$ for carbon determination is the possibility of carrying out surface analysis and analysis of a layer below the surface simultaneously in a single operation, by studying both resonances at a given value of proton energy.

The authors are much indebted to Dr. G. LAGERBERG, Sandvikens Jernverk AB, for kindly providing the steel samples. The financial support from Styrelsen för Teknisk Utveckling, Stockholm, is greatly appreciated.

SUMMARY

The carbon content and depth distribution close to the surface in steel samples at the 0.1–1% level have been studied, by means of proton activation in the energy range 1–4.5 MeV. A Van de Graaff accelerator was used, initiating the nuclear reaction $^{12}C(p,\gamma)^{13}N$ which possesses two resonances at the energies of 0.46 and 1.70 MeV. The technique is of interest in connection with carbonization of iron products.

RÉSUMÉ

Une étude est effectuée sur la teneur en carbone des aciers et sa distribution, au moyen de l'analyse par activation protonique (1–4.5 MeV). Un accélérateur Van de Graaff est utilisé, amorçant la réaction nucléaire $^{12}C(p,\gamma)^{13}N$, ayant deux résonances, aux énergies de 0.46 et 1.7 MeV. Cette technique présente un intérêt en relation avec la carbonisation de produits ferreux.

ZUSAMMENFASSUNG

Es sind die Kohlenstoffgehalte und die Tiefenverteilung dicht unter der Oberfläche von Stahlproben bei Gehalten von 0.1–1% durch Protonenaktivierung im Energiebereich 1–4.5 MeV untersucht worden. Für die Durchführung der Kernreaktion $^{12}C(p,\gamma)^{13}N$, die zwei Resonanzenergien bei 0.46 und 1.70 MeV besitzt, wurde ein Van de Graaff-Beschleuniger benutzt. Das Verfahren ist im Zusammenhang mit Kohlungsprozessen bei Eisenprodukten von Interesse.

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REGULARITIES IN THE DISTRIBUTION OF TTA AND ITS SCANDIUM CHELATE INTO A SERIES OF ETHER SOLVENTS

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Solvent extraction is a powerful separation method, but few theoretical studies have been made on the role of solvent in such methods. Such studies can simplify the selection of the most appropriate solvent for an extraction, and the information is also useful in "solution" chemistry, where the distribution mechanism of a species and the complex formation in the organic phase are investigated.

In the first stage of the present research, it was predicted by means of conventional solution theory that regularities in the distribution coefficient of a certain species between two phases can be connected with the "solubility parameter" of the organic solvent, and the validity of this theoretical treatment was verified experimentally in the distribution of β-diketones and their scandium chelates into the so-called inert solvents[1-3]. Oxygen-containing solvents are widely used not only in ion-association extraction systems but also in chelate systems; in the latter systems, these solvents often cause an enhancement of metal extraction, *i.e.* a synergic effect. Since esters and ketones are polar solvents, application of the same treatment as for inert solvent systems may seem dubious; however, in these solvent systems, dispersion forces predominate in the cohesive energies among molecules[4,5], hence the same treatment should be permissible. Satisfactory results were obtained in alcohol, ester, and ketone solvent systems[6-9]. In view of these facts, the same treatment was expanded to ether solvent systems.

In this work, 2-thenoyltrifluoroacetone (TTA) was chosen as a typical chelating agent and scandium as a representative trivalent metal ion. The distribution coefficients of TTA into various ethers were determined. A regularity in the distribution of TTA was observed in relation to the solubility parameter of ethers, and a correlation between the distribution coefficient of TTA and that of scandium chelate was found.

EXPERIMENTAL

Reagents and apparatus

TTA and scandium-46 were prepared as described previously[8].

The purest solvents commercially available were washed successively with aqueous solutions of potassium hydroxide and of potassium permanganate, and then with redistilled water. The solvent was then dried over calcium chloride or potassium carbonate, and distilled.

U.v., n.m.r., pH and radioactivity measurements were made as described previously[7,8].

Procedure

Distribution ratio of TTA (D_{HA}). This was determined in the same way as before[8], but with ether solvents, the TTA being determined in the aqueous phase by measuring the absorbance at 290 nm. The pH of the equilibrated aqueous phase was also measured.

Since preliminary experiments had shown that distribution equilibrium was achieved within 8 h, a shaking time of 16 h was chosen as a standard procedure. The distribution ratio of TTA was constant over the initital TTA concentration range of 10^{-1}–10^{-3} *M*, and 10^{-2} *M* TTA solution was therefore used. In the case of ethyl ether, the aqueous solution and the solvent were pre-equilibrated with each other before the distribution experiments.

Distribution ratio of scandium (D_M). This was determined as described previously[8], at ionic strength 0.1 for 10^{-6} *M* scandium(III) labelled with ^{46}Sc tracer.

RESULTS AND DISCUSSION

Distribution coefficient of TTA

In inert solvents, TTA exists almost completely in the enol form, whereas in oxygen-containing solvents such as alcohols, esters, and ketones, the keto form is also present. On a theoretical basis, the distribution coefficient of a fixed chemical species of TTA should be discussed, hence the tautomerism of TTA in ether solvents, especially when these solvents were equilibrated with an aqueous phase, was investigated.

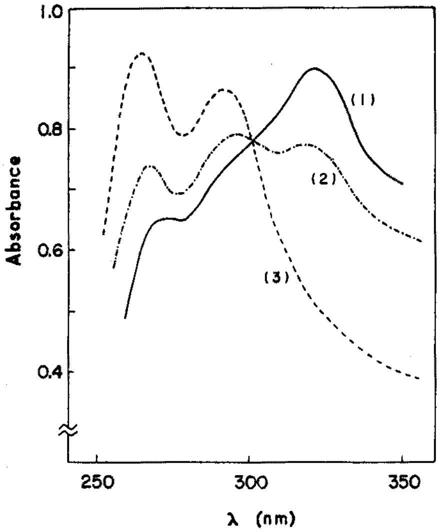


Fig. 1. Absorbance spectra of TTA in ether equilibrated with aqueous solution (pH = 2). $[HA]_{org,init} = 10^{-4}$ *M*; light path = 1.0 cm. (1) Isoamyl ether; (2) isopropyl ether; (3) ethyl ether.

When TTA was dissolved into a pure ether solvent free from water, almost all TTA existed in the enol form, analogous to the case of inert solvents, but a gradual increase in the keto form and/or ketohydrate form of TTA was observed when the organic solvent solution of TTA was shaken with an aqueous phase; this tautomerization attained an equilibrium within several hours of shaking. Typical spectra of TTA in an equilibrated ether phase are shown in Fig. 1. The peaks in the vicinity of 265 and 290 nm may be attributed to the keto form or most probably the ketohydrate form, and the peaks in the vicinity of 320 nm to the enol form. The spectra, which are the sum of the contribution of each species, differ for different solvents. The absorbance at around 320 nm increases when the pH of the aqueous phase exceeds 5. When the ether solutions were equilibrated with the aqueous solution below pH 5, almost the same spectra were obtained. Accordingly, the distribution ratio of TTA determined below pH 5 can be regarded as the reliable one at a fixed keto–enol equilibrium.

As the direct estimation of the enol ratio from u.v. absorption spectra is not easy, an apparent enol ratio for TTA was determined by simple n.m.r. measurement, except for phenyl ethyl ether and benzyl ether, for which the enol ratio could not be determined owing to an interference of solvent itself.

One of the important factors governing the keto–enol equilibrium is the dielectric constant of the medium. Accordingly, in the present systems, which have a rather small dielectric constant, the enol ratio of TTA would be larger than that in the other oxygen-containing solvent systems. As shown in the column 5 of Table I, the enol form of TTA is predominant in ether solvents equilibrated with the aqueous phase of pH below 5. However, the enol ratio of TTA in bis(2-chloroethyl)ether is larger than might have been expected from its larger dielectric constant, 21.

TABLE I

DISTRIBUTION COEFFICIENTS OF TTA AND ITS SCANDIUM CHELATE

(Ionic strength, 0.10 (H,Na)ClO$_4$; 25°)

No.	*Solvent*	δ_{org}	*log* P_{HA}	*Enol ratio*[c]	*log* D_M ($pA = 7.50$)
1	Ethyl ether	7.4[a]	1.91	0.55	1.35
2	*n*-Propyl ether	7.5[b]	1.50	0.71	0.33
3	Isopropyl ether	7.0[a]	1.51	0.68	0.20
4	*n*-Butyl ether	7.6[a]	1.29	0.84	−0.20
5	*n*-Amyl ether	7.6[b]	1.13	0.77	
6	Isoamyl ether	7.3[b]	1.08	0.86	−0.85
7	*n*-Hexyl ether	7.5[b]	1.08	0.91	−0.91
8	Butyl ethyl ether	7.7[b]	1.63	0.69	0.53
9	Phenyl ethyl ether	9.3[b]	1.57		−0.09
10	Benzyl ether	9.2[b]	1.50		0.02
11	Allyl ether	8.1[b]	1.78	0.53	0.70
12	Bis(2-chloroethyl)ether	9.8[a]	1.70	0.66	0.03

[a] Quoted from ref. 15.
[b] Estimated from the HILDEBRAND–SCOTT equation.
[c] Defined as [apparent enol form of TTA]/[total TTA].

When the apparent dissociation constant of TTA ($K_a = 6 \cdot 10^{-7}$)[10], is taken into consideration, the distribution ratio determined below pH 4 is effectively equal to the distribution coefficient of TTA. The values in the column 4 of Table I are the means of at least 6 separate determinations. The distribution coefficients of TTA in ether solvent systems are of the same order as those in the inert solvent[1] and the alcohol solvent systems[6], but are smaller than those in the ester[8] and the ketone solvent systems[9]. As the ether solvents have a relatively small dielectric constant, the smaller distribution coefficient in these systems probably reflects the fact that the role of the ether solvents is closer to that of inert solvents rather than to that of the other oxygen-containing solvents.

Correlation between the distribution coefficient of TTA and the solubility parameter of ether solvents

The relationship between the distribution coefficient of a species A and the solubility parameter of solvent is given by the following equation[1]:

$$\log P_{x,A} = (V_A/2.30\,RT)(\delta_{aq} - \delta_{org})(\delta_{aq} + \delta_{org} - 2\delta_A) \qquad (1)$$

where P_x represents the distribution coefficient of a species A in terms of mole fraction, and V the molar volume. In the present study also, attention was devoted to the enol form of TTA as a fixed species. The distribution coefficient of the enol form of TTA, P_e, can be calculated by the following equation:

$$P_e = (K_e/K_a)[P_{HA}/(1 + K_{org})] \qquad (2)$$

where K_e is the dissociation constant of the enol form of TTA ($K_e = 5 \cdot 10^{-5}$)[10], and K_{org} is the equilibrium constant defined as [keto]/[enol] in the organic phase. Since the enol ratio of TTA may vary with TTA concentration, the enol ratio shown in Table I, which was determined for 0.5 M TTA, would be somewhat different from that for the dilute TTA solution used in the present experiment. However, owing to the lack of reliable data for dilute solutions of TTA, the enol ratio shown in Table I was adopted as an approximate measure. The aqueous phase in the present system was the same as that in the inert solvent system, accordingly an empirical value of 16.3_5 was adopted as a solubility parameter of the aqueous solution[1]. The solubility parameters for several ethers have not been reported and no thermodynamic data for estimation of the solubility parameter of such solvents are available. However, an empirical formula[11] for estimating the heat of vaporization of a nearly non-polar solvent from its boiling point is applicable to ester and ketone solvents[8].

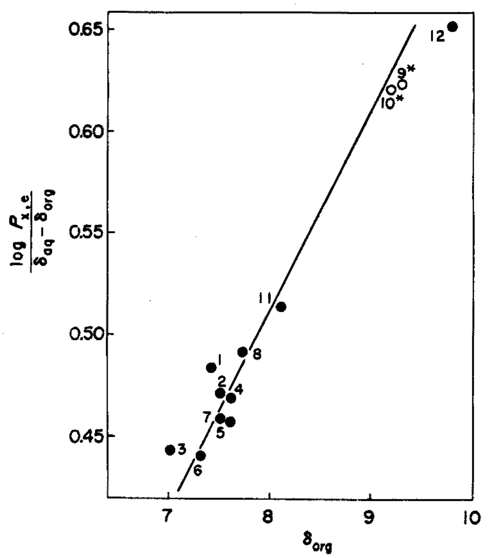
TROUTON's constant for ether solvents shows a value similar to that of normal liquids; furthermore, the physico-chemical properties of the ethers, such as dielectric constant and dipole moment, are closer to those of inert solvents than to those of other polar solvents. Accordingly, an estimation of the heat of vaporization of the ether solvent by the HILDEBRAND–SCOTT formula[11] is permissible. If eqn. (1) is valid in the present system, a plot of $\log P_{x,e}/(\delta_{aq} - \delta_{org})$ against the solubility parameter of ether solvents should be a linear relation. As shown in Fig. 2, the experimental results for ethers are close to a straight line with the slope expected from the molar volume of TTA (160 ml). The plot for bis(2-chloroethyl)ether shows a negative deviation. The enol ratio of TTA in benzyl ether and phenyl ethyl ether could not be determined by a simple n.m.r. measurement; if it is assumed that in these media all the TTA exists as the enol form, the plots for these ethers lie about a straight line. It is clearly indicated that the basicity of these ethers is weakened, because of an electron-withdrawing atom or group, hence the weak interaction between these ethers and TTA may differ from the interactions with other common ethers. Though there are a few exceptions, eqn. (1) is applicable and effective in the present system.

Distribution of Sc–TTA chelate

If adduct formation of chelate with undissociated TTA in the organic phase is considered, the distribution ratio of scandium(III), D_M, can be expressed by[8]:

$$D_M = \frac{P_M\beta_3[A^-]_{aq}^3\{1+\Sigma K_j[HA]_{org}^j\}}{1+\Sigma\beta_n[A^-]_{aq}^n} \tag{3}$$

where D_M is the distribution coefficient of ScA_3, and β_M and K_j are the over-all formation constants for $ScA_n^{(3-n)+}$ and for $ScA_3 \cdot jHA$, respectively. The distribution ratios of scandium were determined at various initial concentrations or at different hydrogen ion concentrations. As shown for a few examples in Fig. 3, the plots of the logarithm of distribution ratio against pA ($= -\log[A^-]_{aq}$) yield straight lines with a slope of about -3.



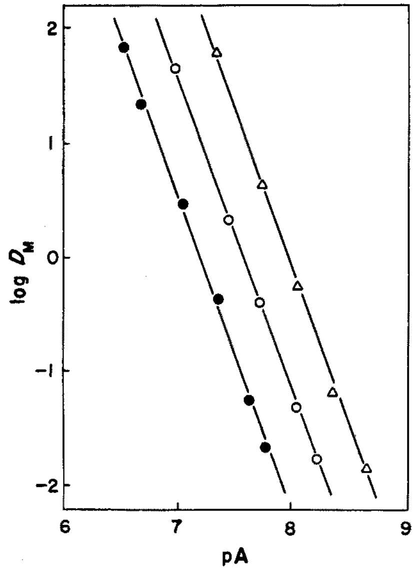


Fig. 2. Correlation between the distribution coefficient of TTA and solubility parameter of ether. * Assuming that enol ratio is 1.0.

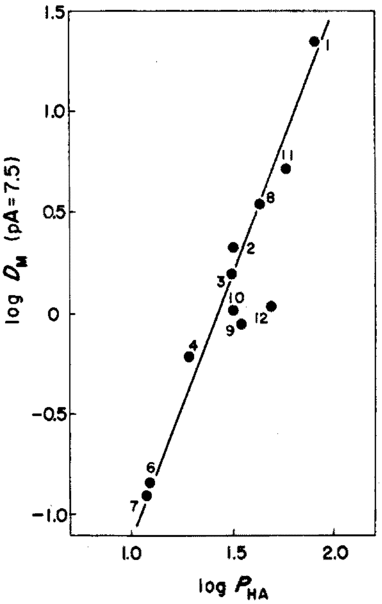
Fig. 3. Distribution ratio of Sc–TTA chelate as a function of pA. Ionic strength, 0.10 (H, Na) ClO_4. (△) Ethyl ether, pH = 2.09; (○) isopropyl ether, $[HA]_{org,init} = 0.01$ *M*; (●) isoamyl ether, $[HA]_{org,init} = 0.01$ *M*.

These facts show that the extractable species is ScA_3 and that adduct formation does not occur under the present conditions, hence eqn. (3) can be simplified. When the distribution ratios at a fixed pA are compared for each solvent, these values should be proportional to the distribution coefficient. Since the distribution coefficient of the chelate is extremely large, it is almost impossible to determine it experimentally. The distribution ratios of scandium at pA 7.50 are compared in Table I.

As has been shown previously for other types of solvent[8], the following correlation can be expected in the ether solvent systems:

$$\log P_M = n \log P_{HA} + \text{const.} \tag{4}$$

The slope, *n*, of this relation is connected with the ratio of the molar volume of a chelating agent to that of the metal chelate[2]; consequently the slope would be near 3 in the distribution of ScA_3. As shown in Fig. 4 the plots of log D_M at pA 7.5 against log P_{HA} give a linear relationship with a slope of 2.8. The plots for phenyl ethyl ether and, especially, bis (2-chloroethyl)ether, show negative deviations, which was also true for the distribution correlation of TTA (*cf.* Fig. 2). However, in consideration of the theoretical basis for eqn. (4), it is necessary to compare the distribution coefficient of the metal chelate with that of the enol form of TTA rather than with the apparent distribution coefficient of gross TTA; this is done in Fig. 5, which shows a slope of 3 for almost all solvents, except bis(2-chloroethyl)ether.



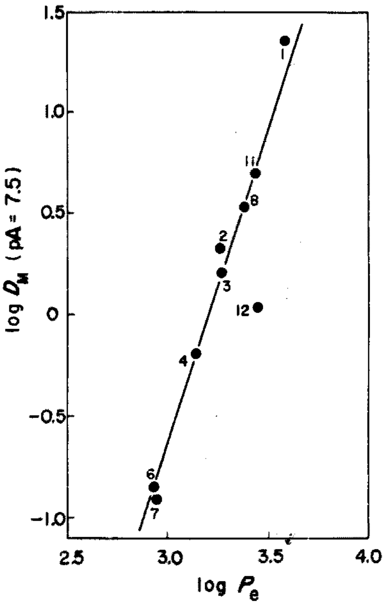


Fig. 4. Correlation between the distribution coefficients of TTA and its scandium chelate.

Fig. 5. Correlation between the distribution coefficients of the enol form of TTA and its scandium chelate.

A smooth linear relationship between two solutes can be expected from the assumption that the nature of the interaction between solute and solvent molecules is the same for two solutes, TTA and its metal chelate. Accordingly, the exceptional deviation for bis(2-chloroethyl)ether suggests that the nature of the interaction of this solute is essentially different; more direct interactions between the chelate and solvent molecule cannot be excluded, although no experimental evidence for a strong coordination of the solvent molecule to the central metal of the chelate could be obtained.

In conclusion, the relationship between the distribution coefficients of two species, a chelating agent and its metal chelate, is clearly observed for the ether solvent systems in an analogous way to the other solvent systems examined. Since the validity of the relationship shown as eqns. (1) and (4) has been confirmed for a number of organic solvents including oxygen-containing solvents, the same treatment should be applicable to general liquid–liquid extraction chemistry, not only in aiding an understanding of the role of the solvent but also as an effective approach to elucidating synergic effects. The same treatment has been applied successfully to the distribution of a divalent metal chelate[12], and the distribution of an adduct with a donating solvent itself or with a neutral ligand such as TBP, has been studied from the same viewpoint[13,14].

The authors are grateful to Professors Y. KITAHARA and T. KANNO for their interest in this study.

SUMMARY

The distribution of a powerful chelating agent, TTA, and its typical trivalent metal chelate, that of scandium(III), between aqueous perchlorate solution ($\mu = 0.1$) and 12 ether solvents was determined at 25°. A good correlation was found between the distribution coefficient of TTA and the "solubility parameter" of the ether solvents, except bis(2-chloroethyl)ether. The distribution coefficient of the scandium chelate (P_M) was compared with that of TTA (P_{HA}), and it was confirmed that the relationship expressed by $\log P_M = n \log P_{HA} + \text{const.}$, is valid for the present system.

RÉSUMÉ

On a examiné la distribution d'un réactif chélatant, TTA, et de son chélate avec le scandium, entre une solution aqueuse perchlorate ($\mu = 0.1$) et 12 solvants, à 25°. Les coefficients de partage du TTA correspondent aux "paramètres de solubilité" des solvants éther, à l'exception du bis(2-chloroéthyl)éther. Le coefficient de partage du chélate de scandium (P_M) est comparé à celui de TTA (P_{HA}), ce qui confirme la relation: $\log P_M = n \log P_{HA} + \text{const.}$, dans ce cas.

ZUSAMMENFASSUNG

Es wurde die Verteilung eines kräftigen Chelatierungsmittels, TTA, und eines seiner typischen Metallchelate, Scandium(III), zwischen wässrigen Perchloratlösungen ($\mu = 0.1$) und 12 Äther-Lösungsmitteln bei 25° untersucht. Es wurde eine Beziehung gefunden zwischen dem Verteilungskoeffizienten von TTA und dem "Löslichkeitsparameter" der Äther-Lösungsmittel, mit Ausnahme von Bis(2-chloräthyl)-äther. Der Verteilungskoeffizient des Scandiumchelates (P_M) wurde mit dem von TTA (P_{HA}) verglichen, und es wurde die Gültigkeit der Beziehung $\log P_M = n \log P_{HA} + \text{const.}$ für dieses System festgestellt.

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A RAPID POLAROGRAPHIC DETERMINATION OF SULPHIDE

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Many analytical procedures have been used for the determination of sulphide ion in aqueous solution, but most of these possess various disadvantages. In direct polarographic methods, the sulphide ion leads to a well-defined anodic wave either at the dropping mercury electrode[1-3] or at the surface of a hanging-drop mercury electrode[4]. Although the sensitivity of the dropping mercury electrode is poorer than that of the hanging drop mercury electrode, the reproducibility of the D.M.E. is greater and experimental conditions require less rigorous control. However, the anodic current method is not entirely satisfactory for quantitative work[2].

Recent polarographic studies[5] in this laboratory have demonstrated that strict stoichiometry is observed for the reaction between methylmercury(II) iodide (MeHgI) and soluble sulphides in water. The present work describes the application of this method to the rapid, highly selective, and sensitive determination of sulphide.

EXPERIMENTAL

Apparatus

Current–voltage determinations were made with a Tinsley Mark 17/4 recording polarograph as described elsewhere[6]. All $E_{\frac{1}{2}}$ values quoted in this paper were measured relative to the saturated calomel electrode.

Reagents

Methylmercury(II) iodide and sodium sulphide solutions were prepared as described previously[5,6]. Other chemicals were of analytical-reagent grade.

Methods

Stock solutions of MeHgI (either $4 \cdot 10^{-4}$ *M* or $4 \cdot 10^{-5}$ *M*) were made up with doubly de-ionised water and contained 0.01% gelatin, 0.1 *M* potassium chloride, and *ca.* 0.03 *M* tris(hydroxymethyl)aminomethane buffered at pH 9.2.

A typical experiment consisted of placing a known volume (*ca.* 10 ml) of the MeHgI solution into the 20-ml polarograph cell. After the solution had been outgassed for 5 min with nitrogen, the gas stream was passed over the surface of the solution while the current–voltage curve was measured. Then an accurately measured volume (0.50 or 1.00 ml) of sodium sulphide solution was added to the solution and the above procedure was repeated. Successive additions of this type lead to a curve[5] which could be used as a calibration graph. Stock solutions of sodium sulphide were analysed by the standard iodimetric method[7] immediately after polarographic measurements.

The effect of interfering anions was determined by adding 1 ml of the appropriate salt solution to a mixture containing 10 ml of MeHgI solution and 1 ml of sodium sulphide solution. The polarogram thus obtained was compared with a "blank" solution which was identical except for the replacement of the interfering salt solution by water.

In all cases the current arising from reductive fission of the mercury–iodine bond of MeHgI (*i.e.* the "first wave", $E_{\frac{1}{2}} = -0.45$ V) was measured at 20°. This current was corrected for volume change in cases where the sulphide solution was added step-wise to an MeHgI solution.

RESULTS AND DISCUSSION

Polarographic measurement of MeHgI

As the method relies on accurate measurement of the residual MeHgI via the current arising from its first polarographic wave ($E_{\frac{1}{2}} = -0.45$ V), a linear relationship between MeHgI concentration and diffusion current is essential. Such a relationship has earlier[6] been established down to a MeHgI concentration of $1 \cdot 10^{-4}$ *M*. In the present study, it was shown that the relationship is linear over the range $4 \cdot 10^{-6}$ *M* to $2 \cdot 10^{-4}$ *M* at pH 9.2. However, it is recommended that the concentrations should exceed $1 \cdot 10^{-5}$ *M*; below this level the instrument sensitivity is such that the precise measurement of a small polarographic wave is difficult, because the "residual current" is similar to the height of the wave itself.

Determination of sulphide

It was shown previously[5] that a 2:1 stoichiometry was obeyed for the reaction between MeHgI and soluble sulphide. With $4 \cdot 10^{-4}$ *M* MeHgI, less than 1 ml of $3 \cdot 10^{-4}$ *M* sulphide was readily detected. Similar measurements were made with $4 \cdot 10^{-5}$ *M* MeHgI and $3.95 \cdot 10^{-5}$ *M* sodium sulphide solution. The results of addition of successive aliquots of the sulphide solution to 10 ml of the MeHgI solution are depicted in Fig. 1. Linear behaviour obviously applies at these low concentrations and there was sufficient change in the magnitude of the first MeHgI wave to allow the deter-

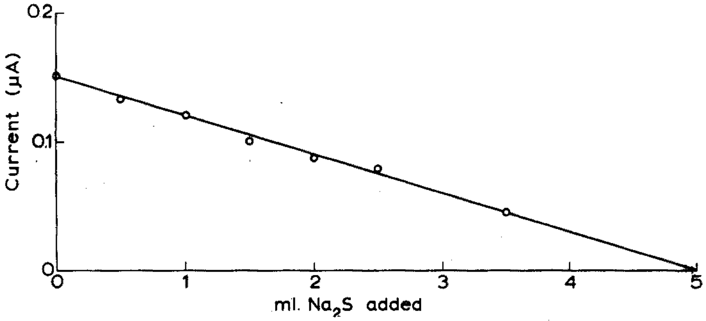

Fig. 1. Amperometric titration of MeHgI ($4 \cdot 10^{-5}$ *M*, 10.0 ml) with sodium sulphide solution ($3.95 \cdot 10^{-5}$ *M*) at pH 9.2 and 20°. Circles represent the current, corrected for volume change, at the first MeHgI wave ($E_{\frac{1}{2}} = -0.45$ V).

mination of 0.5 ml of the sodium sulphide solution (*i.e.* of the order of $2 \cdot 10^{-5}$ millimoles of sodium sulphide or 1 p.p.m. of sulphide). Reproducibility obtained on repeated analysis was within 5%.

Effect of interfering ions

The effect on the MeHgI diffusion current of common anions, including some which are likely to be present as impurities in sulphide solutions, was studied both in the presence and absence of sulphide. The results listed in Table I illustrate the effect of adding water or the appropriate salt solution to MeHgI in the presence or absence of sodium sulphide solution. Of the anions tested, only cyanide significantly affected the MeHgI wave; not only was the magnitude of the current affected, but an extra polarographic wave appeared ($E_{\frac{1}{2}} = -0.75$ V). None of the other ions affected the wave form ($E_{\frac{1}{2}} = -0.46$ V) and the diffusion current did not vary by more than 2%. Similar behaviour was observed when the concentration of all reagents (*i.e.* MeHgI, sulphide and anion) was reduced ten-fold. This lack of interference on the determination of sulphide by all anions tested except the cyanide ion is a distinct advantage over the technique involving measurement of the anodic current arising from presence of sulphide at the dropping mercury electrode; the latter method is also less sensitive to sulphide ion.

TABLE I

EFFECT OF VARIOUS ANIONS ON MeHgI LIMITING CURRENT AND HALF-WAVE POTENTIAL[a]

Reagent	*MeHgI + anion*		*MeHgI + anion + Na_2S*	
	i_d *(μA)*	$-E_{\frac{1}{2}}$ *(V)*	i_d *(μA)*	$-E_{\frac{1}{2}}$ *(V)*
H_2O	1.32	0.46	0.98	0.47
KSCN	1.29	0.46	0.99	0.47
$Na_2S_2O_3$	1.29	0.46	0.97	0.47
Na_2SO_3	1.32	0.48	0.96	0.48
$NaHSO_3$	1.30	0.47	0.96	0.47
Na_2SO_4	1.31	0.47	1.00	0.47
NaCN	0.99	0.47[b]	0.71	0.47[b]
NaI	1.29	0.47	0.97	0.47
NaCl	1.29	0.47	0.96	0.47

[a] 1.0 ml of water or of a $1.0 \cdot 10^{-3}$ *M* solution of the appropriate salt was added to 10.0 ml of $4 \cdot 10^{-4}$ *M* MeHgI. To this was added either 1.0 ml of water or 1.0 ml of $6.0 \cdot 10^{-4}$ *M* sodium sulphide solution.

[b] With a second wave at −0.75 V.

Effect of pH

All previous measurements were made with MeHgI and sulphide solutions buffered at pH 9.2. It is clearly impracticable to operate at a pH below 8, since losses of sulphide as hydrogen sulphide would be appreciable. To investigate the effect of pH on the first MeHgI wave, a stock aqueous solution of MeHgI (5.0 ml) was adjusted to the required pH with acid or alkali and made up to 10.0 ml. The current–voltage characteristics of these solutions are listed in Table II. There was no significant deviation in the magnitude of the diffusion current, but the $E_{\frac{1}{2}}$ values shifted to more negative potentials with increasing pH, tending to a steady value of −0.72 V

TABLE II

EFFECT OF pH ON MeHgI WAVE[a]

Solution	*pH*	*Limiting current (μA)*	$E_{\frac{1}{2}}$ *(V)*
A	7.4	0.83	−0.45
B	9.2	0.85	−0.46
C	10.4	0.85	−0.58
D	11.9	0.84	−0.68
E	12.4	0.86	−0.71
F	12.6	0.83	−0.72
G	12.7	0.83	−0.72

[a] The pH of 5.0 ml of $4 \cdot 10^{-4}$ *M* MeHgI solution was adjusted with hydrochloric acid or sodium hydroxide and the volume was made up to 10.0 ml with water.

at high pH. The addition of 1.0 ml of an aqueous sodium sulphide solution to solutions A, B and G resulted in identical decreases in the height of the MeHgI wave (to 0.61 μA) and no change in the $E_{\frac{1}{2}}$ value. It is thus concluded that this method of sulphide ion analysis may be conducted at any pH above 8.

Mr. B. G. STEVENS is thanked for technical assistance.

SUMMARY

A rapid polarographic method based on the stoichiometric reaction between methylmercury(II) iodide (MeHgI) and soluble sulphide is described for determination of the sulphide ion in aqueous solution; less than 1 p.p.m. of sulphide ion can be determined with a precision of ±5% or better, at pH values greater than 8. Various common anions, with the exception of cyanide ions, do not interfere.

RÉSUMÉ

On décrit une méthode polarographique rapide pour le dosage des sulfures dans l'eau; elle est basée sur la réaction stoechiométrique entre l'iodure de méthylmercure(II) (MeHgI) et le sulfure soluble. On peut ainsi doser moins de 1 p.p.m. de sulfure avec une précision de ±5% ou mieux. Divers anions communs, à l'exception des cyanures, ne gênent pas.

ZUSAMMENFASSUNG

Es wird eine schnelle polarographische Methode für die Bestimmung von Sulfidionen in wässriger Lösung beschrieben. Sie beruht auf der stöchiometrischen Reaktion zwischen Methylquecksilber(II)-jodid (MeHgJ) und löslichem Sulfid. Weniger als 1 p.p.m. Sulfidionen können mit einer Genauigkeit von ±5% oder besser bei pH-Werten grösser als 8 bestimmt werden. Mit Ausnahme von Cyanidionen stören die üblichen Anionen nicht.

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POLAROGRAPHY OF SOME SULPHUR-CONTAINING COMPOUNDS

PART XVI. POLAROGRAPHIC AND SPECTRAL INVESTIGATION OF ACID-BASE EQUILIBRIA IN AQUEOUS SOLUTIONS OF 2-THIOBARBITURIC ACIDS WITH SUBSTITUENTS ON SULPHUR

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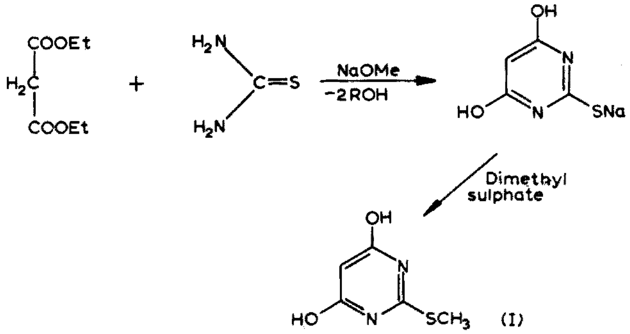
In connection with the study of 5,5'-dialkyl-2-thiobarbiturates and related compounds[1] it proved of importance for the interpretation of the acid-base equilibria involved, to investigate in some detail 2-thiobarbiturates substituted on the sulphur atom. These investigations are discussed in the present paper.

EXPERIMENTAL

Polarographic and spectrophotometric investigations as well as controlled potential electrolysis were carried out with the same equipment and the same type of procedures as those described previously[1].

2-Methylthiobarbituric acid (4,6-dihydroxy-2-methylmercaptopyrimidine) was prepared[2] by condensation of diethyl malonate with thiourea and then by treatment of the product with dimethylsulphate to yield the required thiobarbituric acid (I; m.p. 300°; purity 98–99% by elemental analysis[2]).



(I)

1-Ethyl-2-allylthio-5-(2-methylbutyl)barbituric acid (II) was prepared[3] by reaction of 1-ethyl-5-(2-methylbutyl)-2-thiobarbituric acid with allyl bromide in aqueous sodium hydroxide solution to give the desired product (m.p. 143–44°; purity 99% by elemental analysis[3]).

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RESULTS AND DISCUSSION

Polarographic curves

Polarographic curves of the S-methyl derivative I show a 2-electron wave, the height of which remains constant between pH 2 and 5.3. At higher pH values the height of this wave i_1 decreases in the shape of a dissociation curve with $pK' = 6.5$ (Figs. 1, 2). At pH 5.20, another wave i_2 is observed at more negative potentials, which corresponds to a 6-electron reduction. The height of this wave i_2 also decreases with increasing pH in the shape of a dissociation curve with a pK' value practically identical to that of wave i_1. The ratio of wave-heights i_1:i_2 is independent of the concentration of compound I.

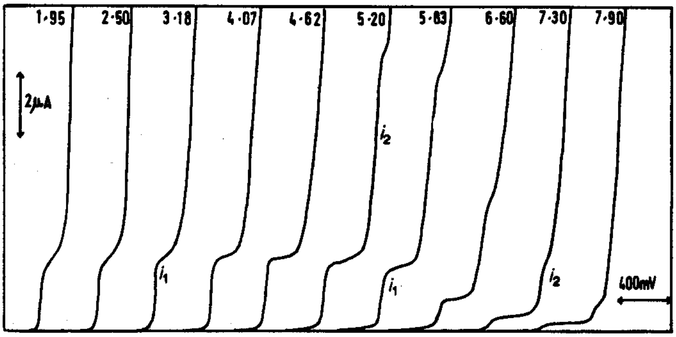


Fig. 1. pH dependence of waves of $5 \cdot 10^{-4}$ *M* 2-methylthiobarbituric acid. pH given on polarogram; Britton–Robinson buffers; curves starting at −1.0 V.

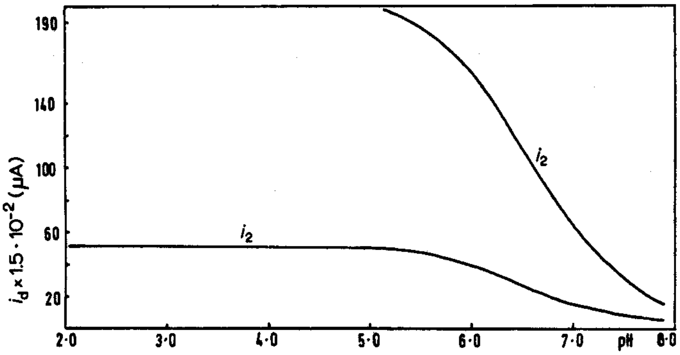


Fig. 2. pH dependence of limiting currents of 10^{-4} *M* 2-methylthiobarbituric acid. Britton–Robinson buffers.

The half-wave potentials of wave i_1 are pH-dependent: the $E_{\frac{1}{2}}$–pH plot shows three linear parts (Fig. 3) with an intersection at pH 4.8 corresponding to pK_1 and another at pH 6.5 which corresponds to pK_1'. The slopes of the three linear parts are 0.058 V/pH, 0.088 V/pH and 0 V/pH. The half-wave potential of wave i_2 is pH-independent below pH 6.6 and is shifted by about 50 mV/pH at higher pH values.

No reduction waves appear above pH 7.9, but in this region a 1-electron anodic wave is observed, the height of which is pH-independent between pH 7 and 11.5. The half-wave potential of this wave is shifted to negative potentials with increasing pH (Fig. 3). At lower pH values only a small anodic adsorption pre-wave limiting at $5 \cdot 10^{-5}$ *M* occurs.

No reduction waves were observed for the 1-ethyl-2-allylthio-5-(2-methylbutyl)-barbituric acid (II).

Electronic spectra

The u.v. spectra of the S-methyl derivative I below pH 4 show an absorption band of medium intensity ($\varepsilon = 9 \cdot 10^3$) at 277 nm, accompanied by a weaker band ($\varepsilon = 7 \cdot 10^3$) at 244 nm. At higher pH values these bands are replaced by a medium-intensity band ($\varepsilon = 8 \cdot 10^3$) at 260 nm, accompanied by a shoulder at 245 nm and another strong band at 210 nm ($\varepsilon = 2 \cdot 10^4$) accompanied by a shoulder at 226 nm (Fig. 4). The decrease of absorbance at 290 nm, and the increase of absorbance at 255 nm or 220 nm have all the shape of a dissociation curve with pK_1 about 4.9. When the pH is increased above about 8, the peak at 260 nm becomes broader and a shoulder appears at about 283 nm.

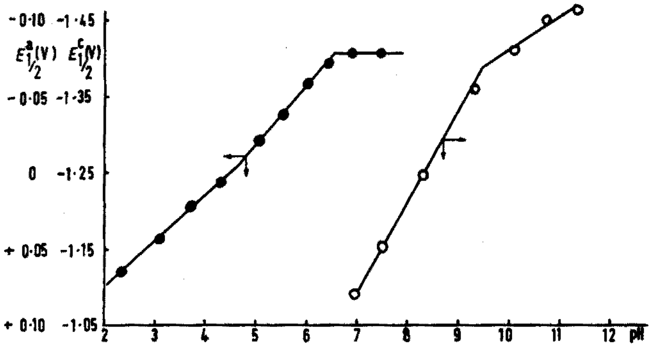


Fig. 3. pH dependence of half-wave potentials of 10^{-4} *M* 2-methylthiobarbituric acid. Britton–Robinson buffers. (●) Cathodic; (○) anodic.

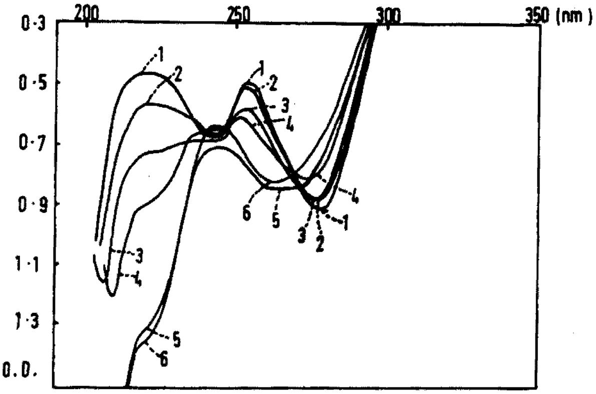


Fig. 4. pH dependence of u.v. spectra of 10^{-4} *M* 2-methylthiobarbituric acid. Britton–Robinson buffers. pH: (1) 2.88, (2) 3.82, (3) 4.41, (4) 4.82, (5) 5.33, (6) 6.11.

The u.v. spectra of the S-allyl derivative (II) bearing an ethyl group on nitrogen shows in strongly acidic media a characteristic band at 276 nm ($\varepsilon > 9 \cdot 10^3$), accompanied by a strong band at shorter wavelength ($\varepsilon > 1.6 \cdot 10^4$, 216 nm). At pH 1–5, relatively weak bands are observed at 253 nm ($\varepsilon = 3 \cdot 10^3$) and at 290 nm ($\varepsilon = 5 \cdot 10^3$) accompanied by a shoulder at 270 nm. Above pH 6.8 a band of medium intensity ($\varepsilon = 9 \cdot 10^3$) is observed at 270 nm accompanied by a shoulder at 283 nm and a strong band at 218 nm ($\varepsilon = 2.3 \cdot 10^4$). No further changes were observed up to pH 13.

The plot of the absorbance at 270 nm or 220 nm against pH has the shape of a dissociation curve with pK about 6.1.

Controlled potential electrolysis

When controlled potential electrolysis of a $1 \cdot 10^{-3}$ M solution of compound I in Britton–Robinson buffer pH 4.4 was carried out at the potential of the limiting current of wave i_1, the height of this wave at -1.26 V decreased and a new wave was formed at -1.6 V. The height of this wave at -1.6 V after exhaustive electrolysis was similar to that of wave i_1 before commencement of the electrolysis. Even when the characteristic odour of sulphur compounds was observed during electrolysis, no anodic waves of hydrogen sulphide or mercaptans were observed in the sodium hydroxide solution into which the gas leaving the electrolysis cell was scrubbed. During electrolysis the u.v. absorbance band of compound I at pH 4.4 at 277 nm gradually decreased. This decrease was accompanied by an increase of a new band at 253 nm with a shoulder at 240 nm.

Reduction scheme

The following scheme (1)–(3) can be proposed for the reduction of compound I:

$$\mathrm{HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} + \mathrm{H}^+ ; \qquad \mathrm{p}K_1 \tag{1}$$

$$\mathrm{HA} + 2e \xrightarrow{E_1} \mathrm{P}_1 ; \qquad i_1 \tag{2}$$

$$\mathrm{P}_1 + 6e \xrightarrow{E_2} \mathrm{P}_2 ; \qquad i_2 \tag{3}$$

This scheme is in agreement with the observed pH dependence of both the wave-heights and half-wave potentials of the cathodic waves provided that the form C remains electroinactive in the available potential range.

Below pH 5.2, form HA is reduced in a 2-electron step followed by a 6-electron transfer, which is overlapped by hydrogen evolution at lower pH values. Above pH 5.2, the rate of protonation with rate constant k_{-1} is no longer fast enough to transform all the thiobarbiturate from form C into HA. The wave i_1 of the form HA decreases and its height becomes limited by the rate of the chemical reaction with constant k_{-1}. On the assumption that protonation (1) takes place at the electrode surface as a volume reaction[4], it is possible from the difference between the spectrophotometrically determined value p$K_1 = 4.80$ and the inflexion of the i–pH plot (p$K_1' = 6.5$) to calculate[5] the value of the rate constant k_{-1}. The estimated value was of the order 10^8 and indicates that the assumption of a volume character for reaction (1) is reasonable.

No information is available on the reduction products formed in the 6-electron step i_2 apart from the fact that only the reduction product of the form HA but not C can undergo furhter reduction.

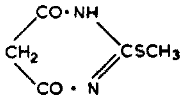
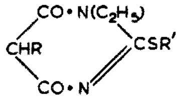
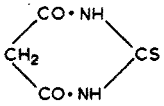
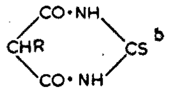
Acid–base equilibria involved

The change of absorption spectra of the S-methyl derivative I and the S-allyl compound II with pH indicates the existence of an acid–base equilibrium in the medium pH range. For compound I this is further supported by the intersection of the two linear sections of the $E_{\frac{1}{2}}$–pH plot at pH 4.8. These compounds can either be protonated on one of the nitrogen atoms or lose a proton from the CH-group in position 5 (or from the enol form).

The weak absorbance bands at 244–253 nm and strong absorbance bands at 277–290 nm observed for compound I at pH 0–4 and for compound II at pH 1–5 can be attributed to a monoprotonated form rather than to an uncharged molecule. This is supported by comparison with the bands of form HA of the 5,5′-disubstituted-2-thiobarbiturates[1] and also of bands of 2-thiobarbituric acid (III) and its 5-(1-methylbutyl) derivative (IV) (Table I) which must correspond to species enriched by two protons when compared with the anion. Furthermore, the polarographic reduction of the S-methyl derivative I in one 2- and one 6-electron wave resembles the reduction of the monoprotonated form HA of 5,5′-dialkyl-2-thiobarbiturates[1]. Finally, it can be observed for all compounds I–IV that an increase of pH from the region in which form HA predominates to the pH region where form C predominates results in

TABLE I

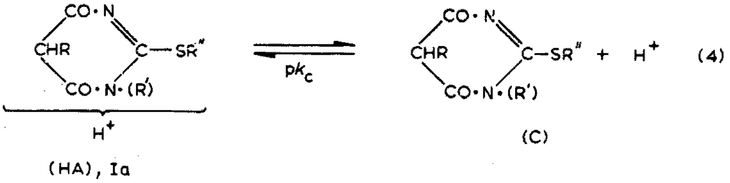
COMPARISON OF ELECTRONIC SPECTRA OF SELECTED FORMS OF THIOBARBITURATES ($\varepsilon \cdot 10^4$)

No.	*Compound*	H_2A		*HA*		*C*		*D*	
		λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
I		—	—	244 277	0.7 0.9	210 245s 260	2 ≏0.2 0.8	—	—
II	 [a]	216 276	>1.6 >0.9	253 270s 290	0.3 ≏0.1 0.5	218 270 283s	2.3 0.9 ≏0.2	—	—
III		—	—	235 283	0.9 2.4	243 264 280s	0.8 1.8 ≏0.3	236 260s 283	1.8 ≏0.3 1.3
IV	 [b]	—	—	240 287	≏0.5 >1.2	239 275 290s	1.0 1.8 ≏0.2	234 265s 288	1.8 ≏0.2 1.3

[a] R, $CH_2CH(CH_3)CH_2CH_2$; R′, $CH_2{=}CHCH_2$.
[b] R, $CH_3CHCH_2CH_2CH_3$.

replacement of the strong band at 277–290 nm by another strong band at wavelengths 12–20 nm shorter (Table I). On the other hand, formation of a carbanion–enolate has been shown[6] to be accompanied by an increase of a strong absorption band at *longer* wavelengths than that corresponding to the uncharged molecule. This indicates that the formation of a carbanion–enolate is not involved in the increase of the band for species C.

The acid–base equilibria of compounds I and II in the medium pH range can thus be formulated by eqn. (4):



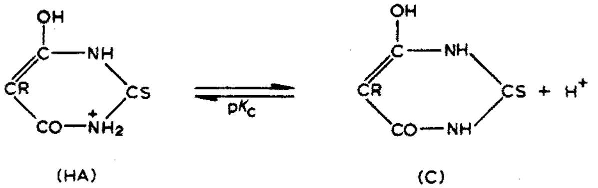
Formation of new bands observed for compound II in strongly acidic solutions can be ascribed to the diprotonated form. No changes in spectra of compounds I and II in strongly alkaline media, which would indicate anion formation, were observed. Spectra of I and II are quite analogous, so that substitution of S-allyl and N-ethyl does not on the whole change participation of predominant forms.

It is realised that the structures given in eqn. (4) represent only one of the possible tautomeric forms. Whereas comparison of the spectra with those for 1,3-dimethyl-5,5′-di-*n*-propyl-2-thiobarbituric acid in which the keto form is fixed, enabled attribution of the most probable structure to 5,5′-dialkyl-2-thiobarbiturates[1], the available experimental evidence does not allow an estimate of the contribution of enol forms to structures HA and C of compounds I and II. So far, it has been impossible to decide whether all absorption bands and shoulders observed correspond to one form, or to a mixture of several forms.

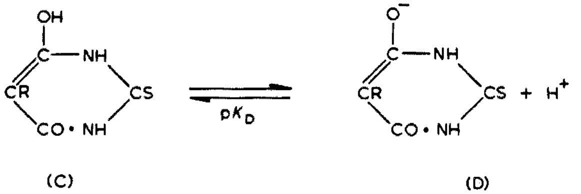
The extinction coefficients of bands at 277 and 290 nm for compounds I and II are considerably lower than those for the corresponding bands of forms HA at 283–292 nm for all other compounds with an unsubstituted CS group (Table I). For 5,5′-dialkyl derivatives[1] these bands were attributed to the thioxo form (with C=S). The similar wavelengths and character of the spectra and lower extinction coefficients can be interpreted by involvement of the *d*-orbital resonance in the form HA of compounds I and II.

There remains to discuss the acid–base equilibria in solutions of unsubstituted 2-thiobarbituric acid (III) and the monoalkyl derivative (IV). As indicated above, the first dissociation step observed may be attributed to protonation of a nitrogen. The second dissociation step observed above pH 10 can be ascribed either to the formation of a carbanion–enolate or to the formation of a thiolate form.

Bands of form D at 282 to 290 nm are in the same region and have similar extinction coefficients as other 1,3-diketones[6]. These bands have shorter wavelengths (about 20 nm) and have half the value of the extinction coefficients of the bands of form B of 5,5′-dialkyl-2-thiobarbiturates, for which also the intense band at 235 nm was not observed. The tautomeric form (D) shown in eqn. (6) seems therefore the most probable, but the differences may be quantitative rather than qualitative and contribution of other tautomeric forms in (5) and (6) cannot be excluded:



(5)



(6)

All the acid–base equilibria (4), (5) and (6) are considerably affected by structure (Table II). The pK values can be affected by the polar effects of the alkyl groups and by their effect on the keto–enol equilibria. The observed effects are considerably larger than would be expected for polar effects affecting electron density on one single tautomeric form. The value of pK_C is related to the dissociation constant of the keto form K_{keto} by the relation: $K_C = K_{keto}/(1+[\text{Enol}]/[\text{Keto}])$. If we assume as a first approximation that the dissociation constant of the keto form is only slightly affected by the structural change, it is possible to deduce that in both comparable pairs—I and II or III and IV—the increase in the pK_C value indicates an increase in the enol content.

TABLE II

COMPARISON OF DISSOCIATION CONSTANTS

Compound no.	pK_C	pK_D
I	4.8[a]	>13
II	6.1	>13
III	2.25	10.72
IV	≏1.0	≏12

[a] From $E_{\frac{1}{2}}$–pH plots pK_C=4.8; pK_C' values of 6.5 were obtained both from i–pH and $E_{\frac{1}{2}}$–pH plots.

Contrary to previous interpretation[7] the first dissociation step of thiobarbiturates of type III and IV is not attributed to the formation of a carbanion, but to protonation of the amino group. The previous attribution of pK_1=2.25 would make 2-thiobarbituric acid an unusually strong C-acid, whereas our attribution of pK_2=10.72 to formation of a carbanion–enolate makes this acid little different from numerous other C-acids.

Electroactive forms

The similar pH dependence of waves i_1 and i_2 for compound I to those of waves i_1^{HA} and i_2' for 5,5'-dialkyl-2-thiobarbiturates[1] is a further contribution to the proposal that a monoprotonated form HA is reduced in the first 2-electron step.

The electroinactivity of compound II which bears an alkyl group on nitrogen and one alkyl group on 5-C can be due to the polar effects of these substituents on the

TABLE III

COMPARISON OF METHODS OF ANALYSIS OF THIOBARBITURATES CONTAINING AT LEAST ONE HYDROGEN ATOM ON CARBON-5 AND THOSE SUBSTITUTED ON THE SULPHUR ATOM

Compound	*Anodic polarographic waves*			*Cathodic polarographic waves*				*U.v. spectral bands* [b]	
	Electrolyte	*Conc. range*[a] *(M)*	*Correlation coefficient (r)*	*Electrolyte*	*Conc. range*[a] *(M)*	*Slope of calibration curve* $(\mu A\ mmol^{-1})$	*Correlation coefficient (r)*	*pH*	λ
I	Britton–Robinson buffers, pH 8–10.5	10^{-5} $-1.5 \cdot 10^{-4}$	0.995	Acetate buffer pH 4.6	$5 \cdot 10^{-6}$ $-2 \cdot 10^{-3}$	4.98	0.9999	6.5–9.5	210 nm ($\varepsilon = 2 \cdot 10^{-4}$) 226 nm ($\varepsilon = 1.5 \cdot 10^{-4}$)
II	—	—	—	—	—	—	—	>7	225–235 nm region ($\varepsilon = 10^{4}$)
III	0.1 *M* sodium hydroxide	10^{-5} $-1.2 \cdot 10^{-4}$	0.998	—	—	—	—	13–14	236 nm ($\varepsilon = 1.8 \cdot 10^{4}$)
IV	0.1 *M* sodium hydroxide	10^{-5} -10^{-4}	0.991	—	—	—	—	12–14	235 nm ($\varepsilon = 1.9 \cdot 10^{4}$)

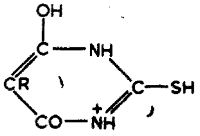
[a] Range of linearity of limiting current–concentration relationship.
[b] Spectral bands most suitable for analytical purposes.

half-wave potential, or due to predominance of an electroinactive form in solutions of II from which an electroactive form cannot be rapidly generated.

The pK value of compound II (pK_1=6.1) and comparison with the electroactive 5,5′-dialkyl-1-alkyl-2-thiobarbiturates (where the corresponding pK value of the HA form is little changed by introduction of alkyl groups on nitrogen in position 1) seem to indicate that the difference in the acidity is not the decisive condition for electroactivity. Keto forms and enol forms can be formed by both species and therefore cannot be used for interpretation of the observed difference. Moreover, predominance of the enol form is assumed to explain the electroinactivity of unsubstituted 2-thiobarbituric acid and is not thus likely to account for the existence of wave i_1. It seems that the keto form can be formed by I but not by II and hence it is assumed that the 2-electron reduction takes place on this form.

The salts with mercury responsible for the anodic waves are seemingly formed by the unprotonated species C, whereas the protonated form HA gives only an adsorption pre-wave.

Along similar lines it is possible to deduce that in 2-thiobarbituric acid (III) and its 5-monoalkyl derivative (IV), the electroinactivity is due to a predominance of an enol form (IIIb), from which the formation of the electroactive keto form is too slow to become significant during the drop-time. Enols proved to be electroinactive in other systems—*e.g.* 1,3-diketones[6].



(IIIb)

The predominance of the enol form (IIIb) in the monoprotonated state HA which will produce an unprotonated enol as the form C is another contribution to the assumption that the protonated keto form in 5,5′-dialkyl-2-thiobarbiturates[1] produces a zwitterion. For different predominant forms, it is namely necessary to assume a different sequence of pK values of individual tautomeric forms.

ANALYTICAL APPLICATIONS

Compound I is the only one which gives reduction waves suitable for the kind of polarographic analysis to which 5,5′-disubstituted and 1,5,5′-trisubstituted thiobarbiturates have been subjected[1]. Acetate buffer pH 4.6 was found most suitable for determination of this species by means of the cathodic wave. Anodic phenomena are observed for all the species except the S-allyl derivative but, in 0.1 M sodium hydroxide where the best-defined waves are found, linearity of the limiting current–concentration relationships ceases at about 10^{-4} M and the half-wave potentials all occur at approximately the same value.

All four thiobarbiturates I–IV give rise to intense u.v. bands with extinction coefficients of the order of 10^4 and, in general, analysis by means of u.v. absorption techniques has somewhat fewer limitations than those of polarography. A summary of the analytical applications is given in Table III.

We would like to thank R. N. Emanuel Ltd. (London) for sample I, and Dr. M. E. Peel (Allen and Hanburys Ltd., Ware, Herts.) for sample II. The authors thank Professor C. L. Wilson for his encouragement in this work and W. F. S. thanks the Northern Ireland Government for a maintenance grant.

SUMMARY

2-Methylthiobarbituric acid (I) and 1-ethyl-2-allylthio-5-(2-methylbutyl)-barbituric acid (II) have protonation constants of 4.8 and 6.1, respectively; protonation of unsubstituted 2-thiobarbituric acid (III) ($pK_C = 2.25$) and its 5-alkyl derivative (IV) ($pK_C \simeq 1.0$) occurs at lower pH values. I is reducible in a 2-electron process, followed by a further 6-electron step; the rate constant of the antecedent protonation is of the order of 10^8 l mol^{-1} sec^{-1}. Compounds II, III and IV do not show cathodic waves; the reasons are discussed. Anodic waves corresponding to formation of mercury compounds are formed by the unprotonated species. Reduction waves of compound I, and u.v. absorption bands and anodic waves of compounds I–IV are suitable for analytical purposes.

RÉSUMÉ

Une recherche polarographique et spectrale est effectuée sur les équilibres acide–base des acides 2-thiobarbituriques, substitués sur le soufre. L'acide méthyl-2-thiobarbiturique (I) et l'acide éthyl-1-allylthio-2-(2-méthylbutyl)-5-barbiturique (II) ont des constantes protoniques, respectivement de 4.8 et 6.1. Le composé I est réductible avec mise en jeu de 2 électrons, puis de 6 électrons. Le composé II, de même que l'acide 2-thiobarbiturique (III) et son dérivé 5-alcoylé (IV) ne donnent pas de vague cathodique. Les vagues de réduction des composés I–IV, de même que leurs vagues anodiques peuvent convenir à des fins analytiques.

ZUSAMMENFASSUNG

2-Methylthiobarbitursäure (I) und 1-Äthyl-2-allyl-thio-5(2-methylbutyl)-barbitursäure (II) haben die Protonisierungskonstanten 4.8 bzw. 6.1; die Protonisierung der unsubstituierten 2-Thiobarbitursäure (III) ($pK_C = 2.25$) und deren 5-Alkyl-Derivat (IV) ($pK_C \simeq 1.0$) tritt erst bei niedrigeren pH-Werten auf. I ist reduzierbar in einem 2-Elektronen-Prozess, dem ein weiterer 6-Elektronen-Schritt folgt; die Geschwindigkeitskonstante der vorhergehenden Protonisierung ist von der Grössenordnung 10^8 l mol^{-1} sec^{-1}. Die Verbindungen II, III und IV ergeben keine kathodischen Stufen; die Gründe werden erörtert. Anodische Stufen, die der Bildung von Quecksilberverbindungen entsprechen, werden durch die nichtprotonisierten Spezies hervorgerufen. Reduktionsstufen der Verbindung I sowie u.v.-Absorptionsbanden und anodische Stufen der Verbindungen I–IV sind für analytische Zwecke geeignet.

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SHORT COMMUNICATIONS

Correlations between ^{31}P n.m.r. chemical shifts and structures of some organophosphorus pesticides

Several recent publications[1-3] have described the usefulness of high-resolution proton magnetic resonance (n.m.r.) for the elucidation of structure of phosphorus-containing organic compounds used as pesticides. Because phosphorus n.m.r. is playing an ever-increasing role in structure characterization and qualitative identification[4,5] of phosphorus compounds, we have examined ^{31}P n.m.r. spectra of a series of organophosphorus pesticidal compounds. Chemical shifts for thirty-seven organophosphorus pesticides have been measured and correlated with the structures of nine classes of these compounds. Empirical correlations describing the relative effects which the atoms adjacent to phosphorus have on the chemical shifts are given for some of these classes. These correlations between ^{31}P n.m.r. shifts and structure are presented for use in qualitative prediction.

Experimental

The 40.5-MHz spectra were recorded with a Varian HA-100 n.m.r. spectrometer. A capillary tube containing phosphorus oxide, used as an external reference, was inserted into the 5-mm n.m.r. sample tube containing the organophosphorus compound. Analytical standards of organophosphorus pesticides were used. Sample solutions are described in Table I. Chemical shifts were measured by the sideband technique using a Wavetek Multipurpose Oscillator Model No. 116. Positive shifts are upfield from phosphorus oxide; negative are downfield. Compounds are listed by their common or trade names; chemical names and commercial sources for these compounds have been given previously by KENAGA[6].

Results and discussion

High-resolution n.m.r. data provide information about the structure of molecules in two ways. The chemical shift data indicate relative degrees of electron screening of the nucleus, and observation of the electron coupled spin–spin interaction provides additional information on structural relationships of the non-equivalent nuclei in a molecule. In this report only the chemical shifts of some organophosphorus pesticides and the effect on these shifts of the atoms directly bonded to phosphorus are considered. Detailed discussions of spin–spin interactions between phosphorus and proton nuclei of substituent groups will follow in a separate report.

The chemical shifts obtained for thirty-seven phosphorus compounds are given in Table I and are grouped according to the various classes of organophosphorus compounds. For the pentavalent phosphorus, where the atoms adjacent to phosphorus are either sulfur, oxygen, nitrogen, carbon, or a combination of the four, the shifts reported are positive. It can be seen from the data in Table I that the magnitude of the shifts for these compounds decreases in the order phosphates, phosphoramidates, phosphonates, phosphorothioates, phosphoramidothioates, phosphonothioates, and phosphorodithioates.

TABLE I

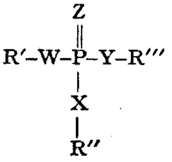
CHEMICAL SHIFTS FOR 37 PHOSPHORUS COMPOUNDS

Compound	*Solvent*	*Chemical shift (p.p.m.)*	*Compound*	*Solvent*	*Chemical shift (p.p.m.)*
Phosphates			*Phosphonates*		
Azodrin	Acetone	118.1	Trichlorfon	Acetone	95.3
Bidrin	Neat	117.6			
Bomyl	Chloroform	118.9	*Phosphorodithioates*		
Ciodrin	Acetone	118.4	Betasan	Chloroform	21.3
Compound 4072	Neat	117.3	Dimethoate (Cygon)	Acetone	15.3
DDVP	Neat	116.1	Disyston	Neat	18.2
Diazoxon	Neat	120.5	Ethion	Neat	20.0
Paraoxon	Benzene	119.7	Guthion	Acetone	18.2
Phosphamidon	Chloroform	117.4	Imidan	Acetone	18.6
Phosdrin	Acetone	118.4	Malathion	Neat	17.5
Ronnoxon	Acetone	117.7	Methyl Trithion	Acetone	15.9
Phosphorothioates			*Phosphoramidothioates*		
Abate	Acetone	46.6	Gophacide	Acetone	56.2
Coumaphos	Neat	50.3	Zytron	Acetone	43.6
Dasanit	Chloroform	50.0			
Diazinon	Neat	52.0	*Phosphoramidates*		
Dursban	Acetone	52.2	Ruelene	Chloroform	104.9
Fenthion	Neat	45.9			
Methyl parathion	Acetone	47.2	*Phosphorotrithioites*		
Nemacide (VC-13)	Neat	49.7	Merphos	Neat	−4.9
Parathion	Benzene	46.0			
Ronnel	Acetone	46.6	*Phosphites*		
Zinophos	Neat	51.2	2,4-DEP	Acetone	−27.1
Phosphonothioates					
EPN	Acetone	28.0			

TABLE II

THE NATURE OF THE ATOMS BONDED TO PHOSPHORUS

Class of compound	*W*	*X*	*Y*	*Z*
Phosphates	Oxygen	Oxygen	Oxygen	Oxygen
Phosphorothioates	Oxygen	Oxygen	Oxygen	Sulfur
Phosphorodithioates	Oxygen	Oxygen	Sulfur	Sulfur
Phosphoramidothioates	Oxygen	Oxygen	Nitrogen	Sulfur
Phosphoramidates	Oxygen	Oxygen	Nitrogen	Oxygen
Phosphonothioates	Oxygen	Oxygen	Carbon	Sulfur
Phosphonates	Oxygen	Oxygen	Carbon	Oxygen
Phosphites	Oxygen	Oxygen	Oxygen	
Phosphorotrithioites	Sulfur	Sulfur	Sulfur	



$$R'{-}W{-}\underset{\underset{\underset{R''}{|}}{\underset{X}{|}}}{\overset{\overset{Z}{\|}}{P}}{-}Y{-}R'''$$

$R' \neq R'' \neq R''' =$ aryl and/or alkyl.

Two trivalent compounds, a phosphite (2,4-DEP) and a phosphorotrithioite (Merphos), were found to have negative shifts, and the magnitudes of these shifts are consistent with those of similar compounds reported in the literature[7].

The chemical shifts of some phosphorothioates including Diazinon, Parathion, and Ronnel were compared with the shifts of their oxygen analogs, the phosphates Diazoxon, Paraoxon, and Ronnoxon. The differences in the shifts for the phosphorothioates in this series were found to be 68.5, 73.7, and 71.1 p.p.m. upfield with respect to the corresponding phosphates. The only structural difference in these compounds is that the sulfur atom in the $P=S$ bond of the phosphorothioates has been replaced with an oxygen atom (Table II). These upfield shifts are contrary to what one would predict on the basis of electronegativity of the atoms[8] but suggest that the $P=O$ bond has more double bond character than the $P=S$ bond[9]. Replacement of the oxygen atom in the R–O–P bond of the phosphorothioates with sulfur (phosphorodithioates) results in an additional upfield shift, again contrary to expectation on the basis of electronegativity and further suggestive of the relative importance of the contributions of double bonded structures such as the $P=\overset{+}{O}R$ type[9].

A nitrogen-for-oxygen substitution results in a more negative shift[10,11] compared to the phosphate class of compounds. This is shown in Table I for the only phosphoramidate examined (Ruelene) and for the two phosphoramidothioates, Gophacide and Zytron. The exact oxygen and sulfur analogs of these compounds, however, were not available for comparison.

A great deal of theoretical and empirical work has been reported relating the chemical shifts to structures of organophosphorus compounds[4,5,12,13]. The n.m.r. chemical shift data for ^{31}P are presented here in qualitative prediction for organophosphorus pesticides and are shown to be potentially useful in their classification according to structural types.

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Determination of low concentrations of organic carbon in phosphoric acid and phosphate rock

The determination of organic carbon in phosphoric acid or phosphate rock becomes difficult when the concentration of carbon is low. Combustion of the sample, with measurement of the carbon dioxide evolved either volumetrically or gravimetrically, is difficult owing to sample size limitations. For example, in a gravimetric analysis, a 10-g sample containing 200 p.p.m. of organic carbon would yield only 7.3 mg of carbon dioxide, hence weighing errors could become significant.

The present communication describes a method, based on dichromate oxidation of the organic carbon, which has been used for analyzing samples containing as little as 50 p.p.m. of organic carbon. The method by MEBIUS[1] for determination of organic carbon in soil has been adapted, with some modifications, to the analysis of phosphoric acid and phosphate rock.

Procedure

Weigh an appropriate sample (*e.g.* 2 g for a sample containing 1000 p.p.m. carbon) into a 125-ml glass-stoppered Erlenmeyer flask. As much as 26 g of sample has been successfully analyzed. Add by pipet 15.0 ml of 0.1 N potassium dichromate (in 24.5%(v/v) sulfuric acid) followed by 10.0 ml of concentrated sulfuric acid. Join the flask to a water condenser and heat on a hot plate until the sample has refluxed for not less than 30 min. After refluxing, cool the flasks in an ice bath and rinse the condensers with deionized water. Then titrate with 0.1 N ammonium iron(II) sulfate solution (in 2.7%(v/v) sulfuric acid) from a 25-ml buret, using 4–5 drops of 0.2%(w/v) N-phenylanthranilic acid, indicator solution (boil 0.2 g of indicator with 100 ml of 0.2 % sodium carbonate solution and filter). The end-point is excellent, the solution changing from purple to green at the equivalence point. A blank containing the reagents is carried through the refluxing procedure.

The sample must also be run for "easily oxidized" compounds and a correction applied to the data, as follows. Weigh the sample into a 250-ml Erlenmeyer flask, pipet 10.0 ml of the dichromate solution into the flask and titrate with the iron(II) solution. The volume of dichromate consumed is divided by the sample weight to give ml g^{-1}. The organic carbon is calculated as follows.

$$\% \text{ organic C} = (A - B - C)\,(N)\,(0.003)\,(100)/D$$

where: A = ml iron(II) solution required for the blank; B = ml iron(II) solution required for the sample; C = ml g^{-1} of sample for "easily oxidized" compounds multiplied by D; D = sample wt, g; and N = normality of the iron(II) solution.

Results and discussions

Several factors were investigated in order to determine the optimal conditions for the analysis.

Need for refluxing. A typical sample of phosphoric acid, P1, was used; this sample contains about 760 p.p.m. organic carbon (determined at optimal conditions). The experiment consisted of pipetting 15.0 ml of 0.1 N dichromate solution into flasks containing about 2.5 g of sample, pipetting various amounts of sulfuric acid into the flasks, and titrating with 0.1 *N* iron(II) solution about 2 h after the sulfuric acid had been added. A blank containing all the reagents was run at each sulfuric acid concentration. Table I shows the data collected.

TABLE I

EFFECT OF SULFURIC ACID WITHOUT REFLUX

H_2SO_4 added (ml)	0	10	20	30	40
Org. C found (p.p.m.)	26[a]	296	402	411	441

[a] This value is probably not correct. The dichromate consumed is most likely that which reacts with species such as iron(II) in the sample, *i.e.*, "easily oxidizable" compounds. The other values are corrected for these compounds.

The increase in p.p.m. carbon found upon adding increasing amounts of sulfuric acid does not indicate that the value of 760 p.p.m. organic carbon would ever be reached with a reasonable volume of sulfuric acid. The conclusion is therefore that refluxing is necessary in order to oxidize the organic carbon completely.

Amount of sulfuric acid needed with refluxing. Varying amounts of sulfuric acid were used with a refluxing time of 30 min. The sample used was Sample No. P2 phosphoric acid, containing about 738 p.p.m. organic carbon (determined at optimal conditions).

TABLE II

EFFECT OF SULFURIC ACID WITH REFLUX

H_2SO_4 added (ml)	0	5	10	15	20
Org. C found (p.p.m.)	390 ± 2	620 ± 7	738 ± 5	734 ± 7	556 ± 3

From the data shown in Table II, one can conclude that 10–15 ml of sulfuric acid can be used when the sample contains about 700 p.p.m. organic carbon. Other data indicated that 10 ml of sulfuric acid is also adequate for samples containing both lower and higher concentrations of organic carbon. Two samples containing 738 and 1600 p.p.m. organic carbon were diluted with pure phosphoric acid and analyzed with 10 ml of sulfuric acid and 30-min reflux times. The results obtained on these diluted samples were reasonably close to the expected values (see Table V).

A 10-ml volume of sulfuric acid was chosen because the blank for this volume was nearer the value obtained in standardizing the iron(II) solution with dichromate. For example, the blank when 10 ml of sulfuric acid was used, was 14.98 ml of iron(II) solution (15.0 ml for the standardization), but 14.16 ml when 15 ml of sulfuric acid was used. When 20 ml of sulfuric acid was used, the blank required 11.77 ml of iron(II) solution. At this concentration of sulfuric acid, the dichromate in the blank was, for some reason, destroyed more quickly than in the sample; this had the net effect of reducing the amount of dichromate consumed by the organic carbon in the sample since the difference between the volume of iron(II) required by the blank and the sample is directly proportional to the organic carbon content.

Time required for refluxing. Sample No. P1 (760 p.p.m. organic C) was analyzed by the given Procedure, except that the reflux time was varied. The data (Table III) indicated that 30 min is sufficient to give complete reaction.

TABLE III

EFFECT OF REFLUX TIME

Reflux time (min)	0	10	20	30	60
C found (p.p.m.)	390 ± 2	705 ± 2	735 ± 3	760 ± 9	762 ± 4

Accuracy and comparison with dry combustion. The accuracy of the method is difficult to measure because no absolute standards are available. Furthermore, no certainly representative standards could be prepared because the form of the carbon in the samples is unknown. The form of the carbon is quite important. Partially oxidized carbon would not have an equivalent weight of 3, as employed in the equation. For example, the applicable equivalent weight of carbon as encountered in the oxalate ion is 12. A standard containing 201 p.p.m. carbon (from oxalate in reagent-grade phosphoric acid) analyzed to give 195, 201, and 198 p.p.m. in a triplicate analysis. Another standard containing 0.201% oxalate-carbon gave 0.198% carbon in a single analysis. In these determinations an equivalent weight of 12 was used.

Since it was important to know both the form of the carbon present in the phosphoric acid and phosphate rock and also the accuracy one could expect from the method, a comparison with another method was needed. This could not be accomplished for low organic carbon samples but was possible for samples containing more than 0.1% organic carbon by using the Leco combustion furnace. Samples of five phosphate rocks and two acids were run by both methods. The data are given in Table IV. The agreement between the two methods is generally quite good and illustrates that an equivalent weight of 3 is generally acceptable for the dichromate method.

TABLE IV

COMPARISON OF DICHROMATE OXIDATION WITH LECO DRY COMBUSTION

Sample	*By* $Cr_2O_7^{2-}$ *method*	*By Leco method*
NBS # 120a	0.22	0.24
1 (phosphate rock)	0.18	0.18
2 (phosphate rock)	0.22	0.21
3 (phosphate rock)	0.28	0.23
4 (phosphate rock)	0.31	0.27
5 (H_3PO_4)	0.16	0.16
6 (H_3PO_4)	0.14	0.15

A comparative method for low organic carbon acid samples was not available. Nevertheless, some samples containing relatively high concentrations of organic carbon were diluted with reagent-grade phosphoric acid and analyzed by the dichromate procedure. For these samples the carbon analyses of the original samples were assumed to be correct. These data are given in Table V.

Reproducibility. Sample numbers P1, P2 and 9 were used to determine the precision of the method (Table VI).

TABLE V

ACCURACY DATA

Sample	*p.p.m. Organic C taken*	*p.p.m. Organic C found*	*Error (Av.)*
7[a]	211	207, 211, 209	0.9
8[a]	59	61, 56, 64	5.7
9[b]	92	87, 87, 90, 90, 90	3.5
10[b]	48	48, 47, 48, 46	1.6

[a] Dilution of sample # 5.
[b] Dilution of sample # P2.

TABLE VI

PRECISION DATA

Sample no.	*p.p.m. Organic C*	*No. of replicates*	*v-50*	*v-99*
P1	760 ± 9	5	760 ± 4	760 ± 24
P2	738 ± 5	6	738 ± 2	238 ± 11
9	89 ± 1.4	5	89 ± 0.6	89 ± 3.4

Effect of chloride and fluoride. MEBIUS[1] found that chloride was a serious interference. The present work confirmed his findings. Chloride as hydrochloric acid was added to a sample containing about 332 p.p.m. organic carbon. With a chloride concentration of 0.8%, an apparent value of 840 p.p.m. organic carbon was found. In addition to causing high results, the chloride made it difficult to see the end-point of the titration.

Since chloride interfered, the effect of fluoride was determined by adding potassium fluorosilicate to a sample of phosphate rock and analyzing by the usual method. As high as 30% potassium fluorosilicate caused no adverse effect on the analysis or the results. This finding is quite important, since practically all the acids and rocks analyzed in this laboratory contain fluoride. Fortunately, all of the phosphate rocks analyzed in this work were low in chloride, and thus did not present a problem.

In summary, the following conclusions can be made concerning this work. The method is quite accurate and precise when one considers the low levels of organic carbon present in the samples. Samples containing as little as 50 p.p.m. organic carbon can be easily analyzed. Species present in the samples which are easily oxidized must be corrected for. Examples of these would be iron(II) and manganese(II) compounds. Chloride is a serious interference if present in greater than p.p.m. concentrations. No effective way was found for eliminating this interference. Fluoride does not interfere.

The method is applicable for determining organic carbon in phosphate rock because inorganic carbon present in the rock (carbonate) is decomposed by the action of the acid, and, therefore, consumes no dichromate.

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A new sensitive spectrophotometric determination of scandium with 4-(2-thiazolylazo)resorcinol

4-(2-Thiazolylazo)resorcinol (TAR) reacts with many metal ions to form colored complexes. The reagent has been used for the spectrophotometric determinations of bismuth[1], cobalt[2], copper[1], nickel[3], niobium[4], tantalum[5], thallium[6], thorium[7] and uranium[8]. The wide application of heterocyclic azo dyestuffs, including TAR, in analytical chemistry has been reviewed by ANDERSON AND NICKLESS[9] and KAWASE[10].

Recently, several chromogenic reagents have been applied for the spectrophotometric determination of scandium as reviewed previously[11,12]. The molar absorptivities of the complexes with some sensitive reagents previously reported are: pontachrome azure blue B (34,000), chromazurol S (27,000), bromopyrogallol red (24,000), xylenol orange (24,000), eriochrome cyanine R (19,000) and arsenazo (17,000). TAR forms a purplish red color with scandium in neutral solution, the complex having a molar absorptivity of 50,600 at 540 nm. In the present communication a new sensitive spectrophotometric procedure for scandium with TAR and its application for trace quantities of scandium in silicate rocks are reported.

Experimental

Apparatus and reagents. A Hitachi recording spectrophotometer (model EPS-3T) with 1-cm quartz cells was used for recording the absorption spectra, and a Shimazu spectrophotometer (model QR-50) for absorbance measurements. A glass electrode pH meter (Toa-dempa model HM-5A) was employed for pH measurements.

0.1% TAR solution was prepared by dissolving TAR in dioxan. A stock solution containing 0.919 mg of scandium per ml of 0.1 *M* hydrochloric acid was prepared and used after appropriate dilution. Buffer solution was prepared by mixing 50 ml of 1 *M* ammonium hydroxide and 500 ml of 1 *M* ammonium chloride solutions to give a pH value of 8.1. All other reagents used were of analytical-grade purity.

Results and discussion

Absorbance spectra. In the pH range 5.0–9.0, the spectra exhibit pronounced absorbance with a peak at 540 nm (Fig. 1). The maximum absorbance of the complex at 540 nm remained nearly constant over the pH range 7.0–8.5.

Effect of experimental variables. The TAR concentration had no effect on the absorbance when amounts above 1 ml of 0.1% TAR solution were added to 25 ml of buffer solution (pH 8.1) containing 22.0 μg of scandium; the concentration of dioxan was kept constant. Because TAR and the TAR–scandium complex were only partially soluble in water, dioxan was required to increase the solubility of the reagent and complex. The solution became turbid when less than 1 ml of dioxan was added. The absorbance remained constant when 1–3 ml of dioxan was present but decreased on further addition of dioxan, the final volume of the solution being kept at 25 ml. At room temperature the color intensity of the solution increased slightly during the first 90 min after the addition of the reagent, and then remained constant for at least several hours.

Conformity to Beer's law. Beer's law was obeyed over the concentration range 0.12–1.6 p.p.m. scandium at pH 8.1 and 540 nm. The sensitivity of the reaction was 0.001 μg Sc cm^{-2} for log $I_0/I = 0.001$. The molar absorptivity of the complex was estimated to be 50,600 at 540 nm.

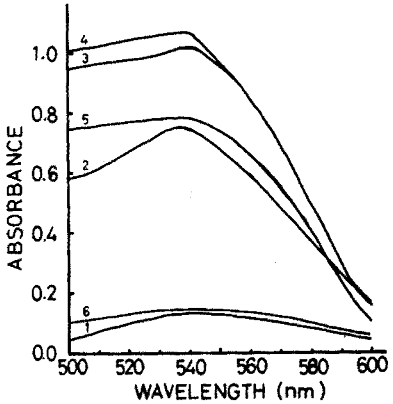

Fig. 1. Absorbance spectra of TAR–scandium complex measured against a reagent blank at various pH values: (1) 4.96, (2) 6.01, (3) 6.65, (4) 8.21, (5) 9.01, (6) 10.23.

Composition of the complex. The molar ratio[13], continuous variation[14] and slope ratio[15] methods unequivocally indicated the formation of a complex containing 1 mole of scandium to 3 moles of the reagent at pH 8.1 and 540 nm.

Recommended procedure

Place a solution containing 3–40 μg of scandium in a 25-ml volumetric flask, and add 2 ml of 0.1% TAR solution. Adjust the pH to 8.1 with 5 ml of the buffer solution, and dilute to 25 ml with water. Measure the absorbance of the solution at 540 nm against the corresponding reagent blank after mixing and standing for 90 min.

Study of interferences

Table I summarizes the results of an interference study with many cations under the above conditions. Tolerance limits are indicated by concentrations of the

TABLE I

CONCENTRATIONS OF CATIONS CAUSING ±5% ERROR IN THE DETERMINATION OF SCANDIUM (0.88 μg ml^{-1})

Cation	*μg ml^{-1}*	*Cation*	*μg ml^{-1}*
Al(III)	0.12	La(III)	0.4
Be(II)	0.2	Ni(II)	0.12
Ce(IV)	1.0	Sm(III)	0.4
Co(II)	0.12	Th(IV)	0.4
Cr(III)	0.12	U(VI)	1.0
Cu(II)	0.2	Y(III)	0.12
Fe(III)	0.2	Yb(III)	0.2
Ga(III)	2.0	Zn(II)	0.2
In(III)	0.12	Zr(IV)	1.0

cations causing errors of more than ±5% in the absorbance of 0.88 p.p.m. of scandium. Chloride, nitrate, sulfate and thiocyanate did not interfere, but large amounts of borate and tartrate interfered. Phosphate must be absent.

Because of the many interferences, a preliminary separation is necessary before the determination of scandium, and this may be effected by a specific anion-exchange chromatographic method in dilute sulfuric acid–ammonium sulfate media[16]; scandium is selectively eluted with 0.1 *M* ammonium sulfate–0.025 *M* sulfuric acid solution from a Dowex 1-X8 (sulfate-form) column.

Determination of scandium in silicate rocks

A complete ion-exchange chromatographic procedure for the separation of small quantities of scandium from various types of silicate rocks has previously been described[17]. After decomposition of a rock sample (0.5–1.0 g) by means of perchloric–hydrofluoric acid digestion, traces of scandium were separated from interferences by a successive cation- and anion-exchange chromatographic technique in acid–ammonium sulfate media and anion-exchange in hydrochloric acid. Scandium was then determined spectrophotometrically with TAR. The results of triplicate determinations of scandium in three types of rocks are given in Table II, and they are compared with those obtained by an arsenazo method[17].

TABLE II

DETERMINATION OF SCANDIUM IN SILICATE ROCKS

Rock sample	*Sc (p.p.m.)*	
	TAR method[a]	*Arsenazo method*[b]
Basalt	35.4 ± 1.3	34.7 ± 1.2
Andesite	19.5 ± 0.7	20.7 ± 1.3
Quartz diorite	10.9 ± 0.5	11.9 ± 1.2

[a] Average of 3 determinations with standard deviations based on the range.
[b] Average of 8–12 determinations.

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Sampling device for fixed volumes from reaction mixtures

The apparatus described here is designed to withdraw samples of fixed volume from reaction mixtures at various temperatures. The maximum working temperature is governed by the boiling points of the components of the reaction mixture.

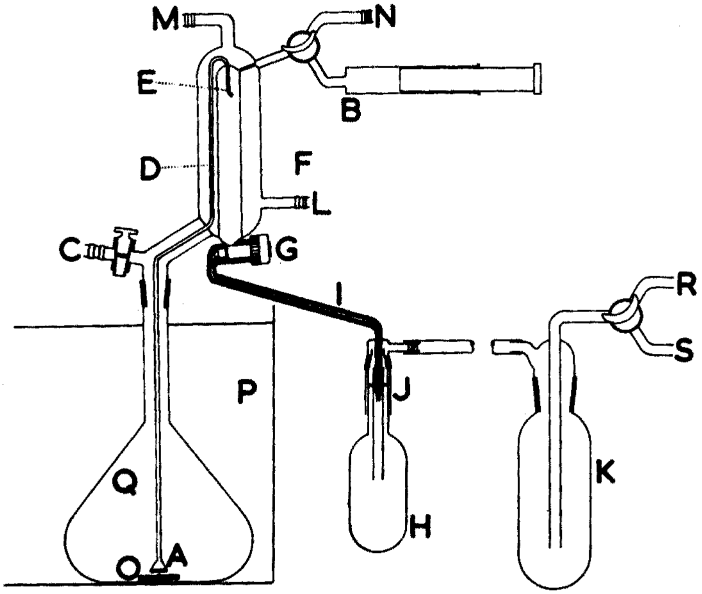

Fig. 1. Sampling device and accessories. (A) Filter disc; (B) syringe (20 ml); (C) pressurised inert gas supply or pressure equilibration; (D) sample elevating tube; (E) automatic levelling device; (F) measuring space; (G) "Rotaflo" stopcock; (H) cooled ampoule; (I) sample outlet tube; (J) sampling head; (K) cooled trap; (L) thermostated water inlet; (M) thermostated water outlet; (N) atmosphere or inert gas supply; (O) magnetic stirrer; (P) thermostated bath; (Q) reaction vessel; (R) outlet to fume cupboard; (S) to vacuum reservoir through constricted tube.

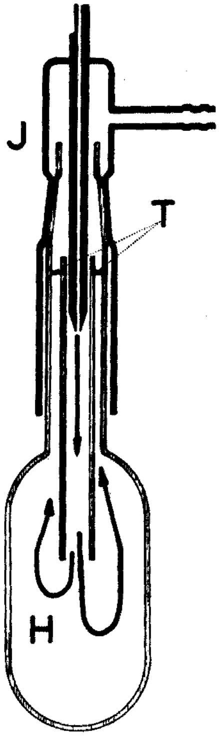

Fig. 2. Details of sampling head. (J) Sampling head (black); (H) ampoule (shaded). The inner tube is fixed by two small glass rods (T). The arrows indicate the flow of sample vapour.

The device (Fig. 1) has the following advantages. Samples may be obtained from both homogeneous and, if fitted with a filter disc (A), heterogeneous (solid/liquid) systems. The apparatus may be operated under an inert atmosphere. Moreover, in homogeneous systems, a sample may be taken from the reaction vessel and stored in a tube (F) at the reaction temperature for the desired reaction time. Volatile radioactive compounds may be sampled safely by use of an output head (J).

Operation

The liquid from the reaction vessel is transferred, via the automatic levelling device E, into the measuring space F by application of suction at B or pressure at C. On releasing the pressure or vacuum, the excess of liquid drains back into the reaction vessel. The liquid sample is delivered by opening the "Rotaflo" stopcock G. Any residual liquid in tube I is expelled by applying pressure from syringe B, which is connected by a 3-way tap to the atmosphere or a supply of inert gas.

When volatile and radioactive compounds are involved, the samples are collected in the cooled ampoule H, thus preventing losses by evaporation as well as minimising any health hazard. The volatile compounds are trapped on the walls of the inner tube as shown in Fig. 2. Changing of ampoules is accompanied by the application of a vacuum through trap K and sampling head J, thus preventing escape of radioactive materials to the atmosphere.

The precision and reproducibility of the apparatus have been checked by collecting and weighing 10 samples each of "Analar" benzene, deionised water and an aqueous 0.03% solution of detergent. The results of these tests are shown in Table I.

TABLE I

PRECISION OF MEASUREMENT FOR DIFFERENT SAMPLES BY WEIGHING

(10 samples of each liquid were taken)

	Benzene		*Water*		*0.03% detergent*
	23.5°	*50.0°*	*23.7°*	*50.0°*	*50.0°*
Average (g)	6.627085	6.42472	7·54705	7·47106	7·47463
Mean deviation (g)	±0.001245	±0.000554	±0.00236	±0.001802	±0.00229

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A reproducible mercury film electrode

Direct wetting of smooth platinum with mercury is not easily accomplished. The platinum surface must be clean and free from oxides, which can be achieved by an electrochemical treatment[1,2]. In practice, however, the surface is often inadequately cleaned. Consequently, the platinum will not be completely coated and reproducible analytical results cannot be obtained.

These difficulties can be overcome by coating smooth platinum with a thin layer of platinum black in a chloroplatinate solution. Mercury easily wets this type of surface. After an anodic and cathodic polarization in purified solutions of 1 *M* perchloric acid, the electrode is dipped into a mercury pool and is completely covered with mercury. The film thickness is about 5 μm.

Smooth platinum, when polarized anodically is oxidized and forms a well-defined oxide, which is not readily reduced. Platinum black, on the other hand, forms an unstable surface oxide, which can be decomposed rapidly[3]. A platinum black surface can thus be cleaned more quickly and efficiently than a smooth platinum surface.

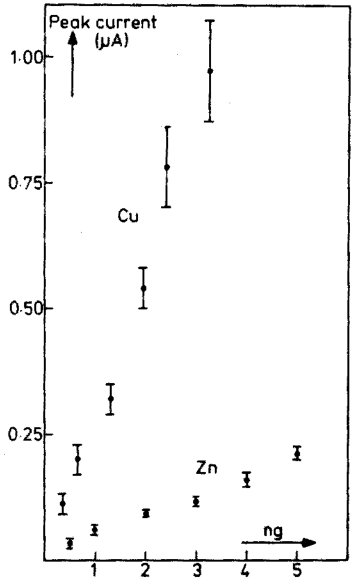

Fig. 1. Precision of the determination of copper and zinc by stripping voltammetry. Electrolyte: 0.02 *M* $HClO_4$. Volume: 50 μl. Electrodes: MFE (vibrating)–S.C.E. Preelectrolysis potential: -1.00 V for Cu, $t = 10$ min and -1.50 V for Zn, $t = 20$ min. Potential scan rate: 2 V min^{-1}. Metrohm Polarecord E 261 R.

These mercury film electrodes have been used for stripping voltammetry in small volumes of solution (50 μl). A platinum wire($\varnothing = 0.2$ mm) is fused into glass; the protruding tip of the wire is coated with mercury as described above. A saturated calomel electrode, serving as the reference electrode, is in contact with the solution via a capillary filled with a solution of 3% agar in 1 *M* potassium nitrate.

Copper ions and zinc ions have been determined in 50 µl of a solution of 0.02 M perchloric acid. Different electrodes and different solutions have been used. In this way concentrations as low as 10^{-7} M, *i.e.* subnanogram amounts, of copper and zinc may be determined with good precision (see Fig. 1).

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Quantitative bromination of aromatic amines

Brominations are frequently used in quantitative analyses of organic compounds which readily react with bromine. A very acceptable source of bromine has been the bromate–bromide solution, which in acidic medium releases bromine. While this reagent is quite stable, brominations are slow and therefore prohibit quick and accurate determinations.

A convenient source of bromine for brominations has been found in pyridinium bromide perbromide (or pyridinium hydrobromide perbromide). PBPB is a brightly colored solid (m.p. 134–135°), each molecule of which readily releases one molecule of free bromine. The ease of handling crystalline PBPB compared with the conventional bromate–bromide solution, and the fast rates of reactions with minimal side reactions, makes PBPB a very desirable reagent for both preparative and analytical work.

DJERASSI AND SCHOLZ[1] have used PBPB for preparative organic brominations of aliphatic and alicyclic ketones in acetic acid. VONA AND MERKER successfully brominated benzene, acetanilide, and anethole[2], and aniline, styrene and phenol[3]. Bromination products of some substituted phenols[4] and aromatic amines[5] have also been prepared with a PBPB reagent. LORETTE *et al.*[6] found PBPB useful in the bromination of flavanones. Photometric titrations are possible for colorless or lightly colored organic compounds, for excess PBPB absorbs strongly at the short wavelength region of the visible spectrum (425 nm). Quantitative spectrophotometric determinations have thus been successfully made for some unsaturated compounds and aromatic ethers and phenols[7].

Apparatus and reagents

The apparatus used in this work was the same as that used earlier[7]. The spectrum of PBPB was determined in a previous study[7]. A wavelength of 425 nm was used earlier and in this study, since the PBPB absorbs in this region and there is no interference from colorless substances being titrated.

The PBPB (commercial grade; Arapahoe Chemical Company) was used without further purification. Standard solutions of PBPB were prepared by weight to between 0.05 and 0.07 *M* in a 10% methanolic acetic acid solvent. To inhibit decomposition of the solution as reported by KRUDENER[8], the reagent was stored in a tightly capped brown bottle. Despite these precautions, it was necessary to standardize the reagent about once a week against primary-standard arsenic trioxide. (Studies over several 2-week periods showed the PBPB solution to decompose at a rate of about 0.05% per day.)

Liquid amines were purified by distillation from zinc dust, and solid amines were recrystallized if necessary, so that their melting points were similar to the literature values. Solutions of the compounds to be titrated were prepared by weight in glacial acetic acid, with the concentrations in most cases being about 0.05 *M*.

For the amine titrations, a mercury(II) chloride catalyst was used; this was made to about 0.05 *M* in methanol. Throughout the project, Fisher Certified glacial acetic acid and methanol were used as solvents without any purification.

General procedure

PBPB standardizations. Periodic standardizations of the PBPB reagent were required. Pipet 10.0 ml of arsenic trioxide solution into 75 ml of methanol in the titration flask. Because the solution is colorless, the initial absorbance can be set at zero. Titrate with PBPB from a 10.0-ml semimicro burette in 1.0-ml increments up to the end-point, and in 0.5-ml increments after the absorbance begins to rise. Absorbance readings stabilize after about 15 sec. Determine end-points graphically using the dilution correction factor. The reaction involved

$$H_3AsO_3 + Br_2 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2Br^-$$

shows that two moles of bromine (or PBPB) are required for each mole of As_2O_3.

Titrations. To 60 ml of glacial acetic acid and 15 ml of methanolic mercury(II) chloride add *ca.* 5.0 ml of the stock solution of the amine to be determined, depending on the concentration of the solution. When the solutions are colorless, the absorbance can be zeroed before the addition of any titrant. (For the colored nitroaniline solutions, the wavelength is set at 450 nm in an attempt to eliminate interfering absorbances.) Add PBPB from a 10.0-ml burette in 1.0- and 0.5-ml increments as in the standardization. In most cases, the titrant is rapidly consumed and the absorbances quickly fall back to zero before the end-point. Near the end-point, however, the reaction rates decrease and longer time periods are required for the absorbances to drop off. After the end-point, the PBPB can be quickly added, the only time factor being that required for stabilization of the readings. Most titrations were completed in 10–15 min.

Results and discussion

Titrations of aniline and various mono-substituted anilines gave excellent results for amine concentrations of about 10^{-4} *M*. Most reactions were fairly fast, making possible accurate determinations in 10–15 min. Table I shows the results of the titrations in terms of percent recovery of the original sample. The number of sites brominated on the aromatic ring was dependent on the ring substituents and their orientations on the ring. The results are consistent with standard electrophilic substitution reactions[9].

TABLE I

RESULTS OF AMINE TITRATIONS

Compound	*Recovery*[a]	*Moles Br_2 incorporated*	*No. of trials*
Aniline	99.94 ± 0.20	3	5
m-Nitroaniline	Undetermined[b]	–	
p-Nitroaniline	99.97 ± 0.45	2	5
o-Chloroaniline	100.43 ± 0.83	2	4
m-Chloroaniline	99.22 ± 0.50	3	3
p-Chloroaniline	100.32 ± 0.16	2	3
o-Bromoaniline	99.08 ± 0.16	2	3
m-Bromoaniline	98.84 ± 0.33	3	3
p-Bromoaniline	99.59 ± 0.60	2	3
o-Toluidine	101.63 ± 0.75	2	5
m-Toluidine	100.00 ± 0.68	3	3
p-Toluidine	99.80 ± 0.40	2	5

[a] % Recovery with standard deviation from the mean.
[b] Reaction rate too slow.

Previous studies have demonstrated uses of PBPB as an analytical reagent for determinations of a wide range of organic compounds, including a series of olefins, phenols, and aromatic ethers, and suggested the application of PBPB to aromatic amine determinations. With successful titrations of a large number of substituted anilines the analytical scope of PBPB as a reagent has been extended. While an earlier study[7] reported the rate of decomposition of the reagent to be about 0.5% daily, this seems to be an overestimation. A decomposition rate of about 0.05% per day was found for this study, and this rate is appreciably less than the 0.2% decomposition reported for a reagent containing bromine in acetic acid used for olefinic titrations[10].

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Determination of fluoride in calcium phosphates with a fluoride-selective electrode

The selective electrode method for the determination of pF values and its use in fluoride analyses is now well known[1,2]. The advantage of the selective electrode method of analysis over spectrophotometric methods has recently been discussed.

The fluoride-selective electrode appears to be specific for fluoride at pH values between 4.5 and 8.5, but the activity of the fluoride ion in solution is affected by changes in the ionic strength of the solution, and by the presence of complexing cations. These disadvantages may be largely overcome by the use of "Total Ionic Strength Adjustment Buffer" (TISAB)[3], made up from acetic acid, sodium chloride, and sodium citrate. The use of large quantities of sodium chloride in this buffer has the disadvantage of introducing relatively large amounts of fluoride present in sodium chloride[4]. Furthermore, the method is not readily usable for the analysis of fluoride present in solids, where prior dissolution is required.

A method for the determination of fluoride in inorganic phosphates where the acid dissolution of the phosphate is an integral part of the buffering of the solution for the determination, is described in this note.

Experimental results and discussion

pF values were obtained with an Orion fluoride-selective electrode connected to a Radiometer PHM 53 selective ion meter. Standard fluoride solutions were made from Analar sodium fluoride. An initial calibration curve was constructed after addition of "TISAB" buffer[3]. A semi-log plot was linear down to *ca.* 0.1 μg ml^{-1} fluoride.

A second calibration curve was constructed in the following manner: 5 ml of a fluoride solution of appropriate concentration was added to 10 ml of *M* hydrochloric acid, and 20 ml of *M* trisodium citrate solution was added to adjust the pH to 5.2–5.3. The pF value of the solution was determined with the electrode. The semi-log plot was again linear to *ca.* 0.1 μg ml^{-1} fluoride (Fig. 1).

Although slight millivolt differences occurred between the two calibration curves, the slopes of the curves were identical, suggesting that no interferences to the determination were likely from the choice of buffer. Addition of sodium dihydrogen ortho-phosphate to the fluoride solution in amounts up to 5000 times [F$^-$] showed no interference with the pF values obtained in hydrochloric acid–citrate media.

The method was used to determine fluoride in various synthetic calcium phosphates, *viz.* $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, and $Ca_5F(PO_4)_3$. The phosphate (100 mg) was dissolved in 10 ml of *M* hydrochloric acid, and 5 ml of deionised water was added, followed by 20 ml of *M* trisodium citrate. The pF value was determined as before. For a number of determinations of fluoride in a single phosphate sample, the range of the fluoride concentration was within ±2%. Similar determinations with "TISAB" yielded a range of ±5%.

Addition of calcium chloride to the standard solutions to give calcium concentrations 5000 times that of fluoride did not cause any detectable interference. It would appear that the formation of a calcium–citrate complex prevents the precipitation of calcium fluoride, which might reasonably be expected under the physical conditions employed.

It has been shown[5] that perchloric acid probably contains less fluoride than any other inorganic acid. The use of this acid might reasonably be considered for dissolution of insoluble phosphates when the levels of extraneous fluoride must be reduced to their lowest level. In this work, the level of fluoride found in calcium phosphates (of the order of 200–500 p.p.m.) was such as to make differences in the pF values obtained too small to be detected by the apparatus used.

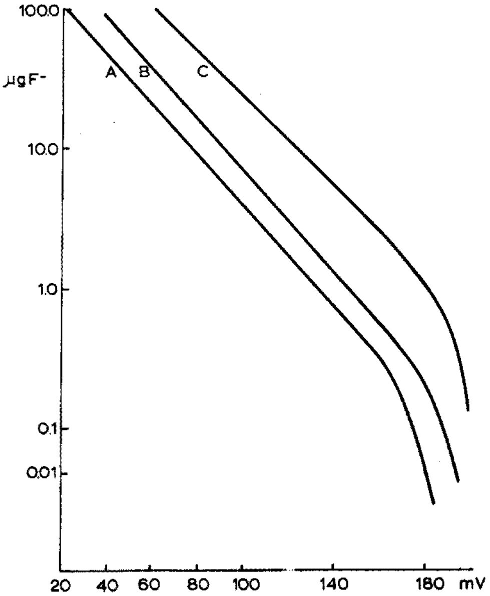

Fig. 1. Calibration curves for fluoride under different conditions. (A) 5 ml 0.2 *M* HCl + 5 ml 0.2 *M* citrate + 1 ml H_2O; (B) 5 ml *M* HCl + 5 ml *M* citrate + 1 ml H_2O; (C) 10 ml *M* HCl + 20 ml *M* citrate + 5 ml H_2O.

In efforts to improve the sensitivity of this method still further, and hence determine lower concentration of fluoride, the work was repeated with 5 ml of *M* hydrochloric acid and 5 ml of *M* trisodium citrate, and with 5 ml of 0.2 *M* HCl and 5 ml of 0.2 *M* trisodium citrate. The volume of water used was also reduced to 1 ml. The results on standard solutions indicated a linear response down to 0.034 μg ml^{-1} and 0.07 μg ml^{-1}, respectively. Neither of these methods significantly reduced the reproducibility of successive determinations on a single sample. The amount of calcium(II) which will be complexed by the citrate will, however, be proportionately less.

This method has been extended to the analysis of dental enamel for fluoride by the following technique. Finely ground enamel (0.2 g) was dissolved in 10 ml of concentrated hydrochloric acid, and made up to 100 ml with deionised water; 10 ml of this solution was added to a mixture of 5 ml of deionised water and 20 ml of *M* trisodium citrate. On 4 separate analyses of the concentrated hydrochloric acid-soluble fraction of a single enamel sample, the fluoride content was determined as 240, 244, 247 and 248 p.p.m., illustrating the reproducibility of this method. Furthermore, it has recently been shown[6] that the use of "TISAB" as the buffer in fluoride determinations on dental enamel invariably leads to an apparently lower result than by other methods. The use of citrate–hydrochloric acid buffers appears to avoid the fluoride loss that occurs with "TISAB".

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Evaluation of 150-W Eimac xenon lamp for atomic fluorescence flame spectrometry*

Most studies in atomic fluorescence spectrometry have been carried out with the aid of electrodeless discharge lamps; these sources produce very intense resonance radiation for some elements and are simple and inexpensive to construct[1,2]. However, electrodeless discharge lamps at the present state of the art do have several disadvantages including instability and relatively short lifetimes for some elements. Continuum light sources, such as xenon arc lamps, have several advantages compared to electrodeless discharge lamps, being generally more stable, longer lived, and useful for more elements. In addition, analytical curves can be predicted[3] quite accurately when continuum sources are used. VEILLON *et al.*[4] first used a 150-W xenon arc lamp of the Osram or Hanovia type and a d.c. electrometer for atomic fluorescence studies. Later ELLIS AND DEMERS[5,6] used a 450-W xenon arc lamp of the Osram or Hanovia type, a mechanized chopper and a lock-in amplifier for atomic fluorescence studies and obtained some excellent limits of detection for Ag, Ca, Co, Cu, Mg, Ni, Tl, and Zn. Other workers who have used the xenon arc lamp for atomic fluorescence studies include DAGNALL *et al.*[7] and MANNING AND HENEAGE[8]. OMENETTO

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AND ROSSI[9] used the background continuum from a mercury vapor discharge arc lamp for atomic fluorescence studies of several elements. All limits of detection previously obtained with continuum sources are substantially poorer than with electrodeless discharge lamps or high-intensity hollow-cathode lamps[3]. Nevertheless, the limits of detection previously obtained are adequate for many analytical studies. Because no thorough study of the limits of detection of many elements with the same continuum source and instrumental set-up has even been performed, such a study was considered necessary.

In this note, limits of detection are given for an Eimac (VL-150-2, Eimac Division of Varian, 301 Industrial Way, San Carlos, Calif. 94070) high-pressure 150-W xenon illuminator and the atomic fluorescence spectrometric system previously described by MANSFIELD *et al.*[10]. The Eimac source is a small, rugged, intense pre-aligned device producing a focused beam of radiation. The source contains a sapphire window with transmission down to 180 nm and an integral reflector. The nominal lifetime of the lamp is 1000 h for 25% degradation in spectral output. With this source at the manufacturer's recommended current level of 12.5 A and the set-up previously described[10], the limits of detection (concentration giving a signal-to-noise ratio of 2) listed in Table I were obtained. Limits of detection obtained with a 500-W Eimac source (500 × 10S) operated at the manufacturer's recommended current of

TABLE I

LIMITS OF DETECTION FOR SEVERAL ELEMENTS IN ATOMIC FLUORESCENCE FLAME SPECTROMETRY WITH THE EIMAC 150-W XENON ARC LAMP

Element	*Wavelength (nm)*	*Limits of detection ($\mu g\ ml^{-1}$)*		
		Eimac source	*Literature continuum source*	*Literature[c] line source*
Ag[a]	328.1	0.05	0.001 (6)	0.0001
Bi[b]	306.8	10.	2. (4)	0.05
Ca[a]	422.6	10.	0.1 (5)	0.02
Cd[a]	228.8	0.08	0.08 (4)	0.000001
Co[b]	240.7	1.	0.5 (5)	0.01
Cu[b]	324.8	0.2	0.02 (6)	0.001
Fe[a]	248.3	5.	1. (8)	0.008
Hg[a]	253.7	100.	—[d]	0.02
Mg[b]	285.2	0.04	0.01 (5)	0.001
Mn[b]	279.5	0.2	0.2 (7)	0.006
Ni[a]	232.0	10.	1. (6)	0.003
Pb[b]	405.7	20.	3.[e] (8)	0.01
Sb[a]	231.1	100.	300. (8)	0.05
Se[b]	196.0	1000.	—[d]	0.8
Sn[a]	303.4	5.	—[d]	0.05
Te[a]	214.3	50.	—[d]	0.05
Tl[b]	377.6	1.	0.07 (6)	0.008
Zn[a]	213.9	7.	0.03 (5)	0.00004

[a] H_2/air unpremixed flame produced with Zeiss total consumption nebulizer burner.
[b] H_2/Ar/entrained air unpremixed flame produced with Zeiss total consumption nebulizer burner.
[c] The limits of detection listed for the line sources are taken from a Table given by WINEFORDNER *et al.*[3].
[d] No limits of detection have been previously listed for these elements excited with continuum sources.
[e] The line used was 283.3 nm.

25 A for Ag, Bi, Ca, Cd, Hg, and Mg were obtained and were comparable (within a factor of 2) with the values listed in Table I. The 500-W source had essentially the same spectral radiance as the 150-W source; because both sources were focused by different optics to illuminate approximately the same flame volume, the flame was essentially being excited by the same spectral radiance from both sources. Therefore no improvement in detection limits resulted with the 500-W source. However, by improved baffling with the present instrumental set-up, with a smaller monochromator slitwidth to reduce the spectral bandpass of the scattered radiation, and with the use of premixed total consumption or premixed laminar flames, lower detection limits than those reported in Table I should result.

For comparison purposes, the best limits of detection previously obtained for elements excited with the Osram or Hanovia type lamps, as well as those obtained with line sources are given in Table I for all elements.

The limits of detection obtained using the Eimac 150-W source for atomic fluorescence flame spectrometry indicate potential use of this versatile system for routine analytical studies for all the elements in Table I except possibly mercury, antimony and selenium. By use of a premixed laminar hydrogen–oxygen–argon flame, it is possible that the limits of detection given could be substantially lowered. By use of a hotter flame, *e.g.* nitrous oxide–acetylene, it should be possible to determine many other elements than those listed in Table I. If the effective color temperature of a continuum source could be increased considerably above 6000°K (the approximate temperature of the Eimac lamp), then the limits of detection should be greatly reduced, particularly for elements with resonance lines below 300 nm. Both the 150-W and the 500-W sources exhibit long- and short-term stability comparable to other analytically employed xenon sources.

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Sample preparation for neutron activation analysis
Deposition of mercury on a plastic matrix

Simpler techniques are needed to concentrate the non-volatile activities in liquid samples before neutron activation assay. Various final-stage techniques[1,2] are available, but these do not involve a simple freeze-drying or vacuum-distillation onto a carrier suitable for direct irradiation and counting. This communication presents a technique which allows the total recovery of non-volatile activities by recovery on a plastic medium; the efficiency of recovery of mercury(II) compounds, such as the nitrate, oxide, and dithizonate, is demonstrated.

Experimental

Radiomercury. ^{203}Hg with a specific activity of 0.45 mCi g^{-1} was obtained by irradiation of samples for 30 min at a flux of $5 \cdot 10^{12}$ n cm^{-2} sec^{-1}, at the Georgia Tech Research Reactor. Standard mercury solutions containing 480 μg of mercury per cm^3 were prepared in 0.05 *M* nitric acid.

Dithizone solution, 0.01%. The dithizone solution was prepared fresh in chloroform every two weeks.

Plastic film liner. Freeze-dry and/or vacuum-distillation flasks were lined on the inside with Handi-Wrap or Saran-Wrap (Dow Chemical Co.). The film was about 17 μm thick. Films were also cast directly in the flasks from a solution of Saran powder dissolved in 70:30 tetrahydrofuran–methyl ethyl ketone. The concentration of Saran in the solvent was adjusted so that after freeze-drying or vacuum-distillation of a sample, the film could be removed from the flask without tearing.

All-glass freeze-drying apparatus. Aqueous mercury samples were freeze-dried (room temperature environment) over a wide acidity range, pH 13.0 to 8 *M* in nitric acid. An all-glass freeze-dry apparatus with two vapor traps was used to avoid corrosion. The cold traps were chilled in a dry ice–acetone mixture and were very effective in preventing corrosive vapors from entering the vacuum pump and gauge. An ultimate vacuum of 20 μm Hg was maintained with the mechanical pump over a 3-month study.

Radioactivity measurements. All measurements were performed at 0.279 MeV. Radio-assays were performed with a Ge (Li) detector and 512-channel ADC pulse-height analyzer. The solid state γ-ray detector has a nominal active volume of 20 cm^3, a system resolution rated at less than 4 keV for the 1.332-MeV ^{60}Co line, and a peak efficiency for the same line of 2.5% relative to a 3 × 3 in NaI detector with a 25-cm source-to-detector distance.

Procedures

The procedures given here refer only to deposition of radioactive mercury(II) compounds on the thin plastic film unless stated otherwise.

Procedure A. Mercury(II) (0–5 μg) was added to a freeze-dry plastic-lined flask containing 20 ml of water with the pH varying from 1.3 to 13.0. After freeze-drying, the film was folded (tweezers and rubber-gloved hands) into a 1 cm × 1 cm pad, encapsulated in scotch tape, and placed directly over the crystal for radioactive assay.

(The film could also be placed in a cylindrical polyethylene tube for irradiation and counting.)

Procedure B. Mercury(II) (0–5 μg) was added to a freeze-dry flask (with no plastic liner) containing 20 ml of water ranging from 8 *M* in nitric acid to pH 13.0 with sodium hydroxide. After freeze-drying, the pH was adjusted to 1.3 with nitric acid and the solution was extracted three times with 2-ml portions of dithizone chloroform. The combined extracts were washed with pH 1.3 water and transferred into a small beaker lined with plastic film. The chloroform was vacuum-distilled at room temperature under soft vacuum followed by complete drying at 20 μm Hg. The film was mounted for radio-assay as in procedure A.

Procedure C. Mercury(II) was added to a flask (no plastic liner and no freeze-drying) containing 20–50 ml of water at acidities ranging from 8 *M* in nitric acid to pH 13.0. If necessary, the pH was adjusted to 1.3 by addition of concentrated nitric acid or sodium hydroxide. The procedure was then the same as in B.

Results and discussion

Table I shows calibration data for determination of mercury(II) in water with initial pH 1.3, by procedure C. The proportionality constant, *K*, is independent of mercury concentration in the range 3–30 p.p.b. mercury. This indicates that the procedure, including deposition of ^{203}Hg–dithizonate on the plastic matrix, is valid throughout the concentration region studied. It is further indicated that encapsulating the flat 1 cm × 1 cm film sandwich in scotch tape resulted in a reproducible sample geometry.

TABLE I

CALIBRATION DATA FOR DETERMINATION OF MERCURY(II) IN 50 cm^3 OF WATER

Sample no.	*μg Hg added*	*P.p.b.*	*Counts h^{-1}*	*Counts h^{-1} μg^{-1} (K)*[a]
1	1.49	29.8	928	623
2	0.451	9.02	275	610
3	0.154	3.08	96	622
			Average =	618 ± 6

[a] Counts = h μg *K*.

The magnitude of the proportionality constant was found to be equal to that obtained by direct transfer of the mercury–dithizonate solution to a small polyethylene tube, evaporating the chloroform, and applying a correction factor to the measurements to take into account the relative counting efficiencies of the different sample geometries. Thus, no mercury was lost by permeation through the plastic film, by volatilization during evaporation of the chloroform, or by spillage of solid mercury dithizonate before encapsulation. Extraction studies indicated that a sufficient excess of dithizone extracted 100% of the mercury in the concentration range 3–30 p.p.b. and ensured efficient removal of mercury from the laboratory glassware.

The non-volatility of the mercury–dithizone complex deposited on the plastic film was studied in detail. Table II shows that the activity of ^{203}Hg–dithizonate (Procedure C, initial pH 1.3) is independent of the vacuum-distillation time used in removing chloroform from the deposited ^{203}Hg–dithizonate and deposited excess dithizone. This indicates that the mercury complex is involatile at room temperature, even for prolonged periods at low pressure.

Table III shows that the deposition principle is also useful for studying losses of mercury by volatilization from various media. The data demonstrate the necessity for a complete characterization of volatility properties of mercury(II) compounds, to prevent serious losses or contamination during chemical processing. The initial acidity of the aqueous samples for runs 2 and 5 was adjusted to 7.7 *M* nitric acid to simulate the required reaction conditions to convert Hg^0, Hg_2^{2+}, and organo-mercury compounds in water to mercury(II) ion. Direct freeze-drying of such high acidity samples resulted in formation of a volatile mercury compound with only 7.7% recovery of ^{203}Hg. Loss of mercury was probably due to formation of undissociated and volatile mercury(II) nitrate at 7.7 *M* nitric acid. Total recovery was still obtained, however, by neutralization of the acid to pH 1.3 followed by direct extraction, as shown in run 5. This indicates that the salt formed in the neutralization process, sodium nitrate, does not interfere with the extraction. When the initial pH was 1.3, the mercury(II) species present were still somewhat volatile, since only 34.4% was recovered. With an initial pH of 13.0, non-volatile mercury(II) oxide was formed, which yielded total recovery after freeze-drying. Table III also shows that at pH 1.3 and 13.0 the same recovery was obtained (runs 3 and 4) whether the evaporation

TABLE II

EFFECT OF VACUUM DISTILLATION TIME ON ACTIVITY OF ^{203}Hg–DITHIZONATE

Time (h)	*Activity*[a] *(counts h^{-1})*	*Recovery (%)*
0[b]	1656	100
2	1685	102
5	1606	97
24	1673	102

[a] 3.2 μg of mercury.

[b] Control sample, vacuum-distilled for a minimum amount of time at soft vacuum. Other samples evacuated at 20 μm Hg pressure.

TABLE III

RECOVERY OF SEVERAL MERCURY(II) COMPOUNDS BY FREEZE-DRYING AND DEPOSITION ON PLASTIC FILM

(4.8 μg Hg added)

Run no.	*20 ml water sample (initial acidity of aqueous sample)*	*Experimental*[a] *procedure*	*Recovery (%)*
1	pH 1.3	C	100[b]
2	7.7 *M* HNO_3	B	7.7 ± 1.0
3	pH 1.3	A,B	34.4 ± 2.5
4	pH 13.0	A,B,C	98 ± 2
5	7.7 *M* HNO_3	C	99 ± 3

[a] All freeze-drying times were 15 h.

[b] Control sample.

led to a dry residue deposited on a film base, or the dried residue was complexed with dithizone and then extracted.

Experiments similar to those described above were carried out with stable mercury isotopes which were subsequently neutron-activated and then radio-assayed. The results obtained showed that neither dithizone nor any of the plastic liners used interfered in the radioactivity measurements.

Lack of interference from a large excess of dithizone is noteworthy. The widely used colorimetric method for mercury with dithizone does not permit appreciable excess of uncomplexed dithizone owing to the light absorption of dithizone itself[3]. Complexation of other metals by dithizone also interferes with the colorimetric method, but is no problem with high-resolution neutron activation analysis. Furthermore, use of excess complexing agent means less time spent on extraction and greater extraction efficiency.

The deposition method has the advantages of rapidity and simplicity, and allows for total recoveries of non-volatile activities. Further applications of freeze-drying and/or vacuum-distillation on plastic films is under study.

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The standardization of sulfatoceric acid with sodium oxalate*

The use of sodium oxalate as a primary standard for cerium(IV) solutions has been discussed by KOLTHOFF AND BELCHER[1]. When iodine monochloride is used as catalyst, the reaction is fast at room temperature, and the end-point can be determined potentiometrically, but with ferroin as the indicator, it is necessary to maintain the temperature between 45° and 50°. Although arsenic trioxide is a satisfactory primary standard for cerium(IV) solutions[1], a less critical procedure based on sodium oxalate was considered to be desirable for check purposes.

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* Taken in part from the dissertation of S. SINGH at St. Louis University.

WHEATLEY[2] recommended the use of 25 ml of 10% manganese(II) sulfate solutions as a catalyst for the titration of 0.01 N oxalate solutions with 0.01 N cerium(IV) solution at room temperature with ferroin as indicator. The method is unsatisfactory at higher concentrations because the indicator changes color to blue with the first addition of cerium(IV) solution; the initial red color slowly returns, and it is necessary to wait after every addition of titrant. The same catalyst was also used by WATSON[3] under similar conditions except that he heated the mixture to 45–50° before titration.

The catalytic effect of manganese(II) in the oxidation of oxalate was utilized in the present work in an attempt to devise an alternative general procedure for the standardization of cerium(IV) solutions.

Reagents

Solutions of cerium(IV) (0.1–0.25 N) were prepared by dissolving a suitable amount of reagent-grade ceric sulfate in 200 ml of 3 M sulfuric acid, and diluting to the desired concentrations.

Primary standard-grade sodium oxalate (99.99–100.01 % purity, National Bureau of Standards) was used. Each sample was dried at 105° before use. The manganese(II) sulfate was Fisher-certified reagent grade.

Procedure

Dissolve a known amount of sodium oxalate equivalent to 30–40 ml of previously prepared cerium(IV) solution, in 25 ml of 2 M sulfuric acid. Add *ca.* 6 g of solid manganese(II) sulfate, and heat to 70° to dissolve the manganese(II) sulfate. Titrate the hot solution with the sulfatoceric acid solution. Titrate initially in stepwise additions using *ca.* 1 ml each time. The local formation of manganese(III) during each addition can be observed; the amber color formed quickly fades on the formation of carbon dioxide. This continues until all the oxalate has been consumed. The final appearance of a yellowish-brown or light amber color produced by the addition of a single drop is taken as the end-point. Thus no additional indicator is needed.

A blank determination showed that a single drop produced the required color change from light pink to yellowish-brown. The latter color results from a mixture of cerium(IV) and manganese(III) in solution. For most titrations the end-point as indicated by the described color change is sufficiently accurate, but a blank titration is recommended for very accurate work.

Discussion

The oxidation of oxalate ions to carbon dioxide is usually visualized as a two-stage process:

$$C_2O_4^{2-} \rightarrow C_2O_4^{-} + e \qquad (1)$$

$$C_2O_4^{-} \rightarrow 2CO_2 + e \qquad (2)$$

Reaction (1) is considered to be the rate-determining step. The oxidation potential of the Ce^{4+}/Ce^{3+} couple is higher than that of the Mn^{3+}/Mn^{2+} couple, and the appearance of an amber color with absorption in the visible spectrum in the same range as manganese(III) prepared by the action of permanganate solutions on manganese(II), makes it clear that manganese(III) is formed as an intermediate. The various reactions and equilibria during the oxidation may therefore be summarized as follows:

$$Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+} \tag{3}$$

$$Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+} + C_2O_4^{-} \tag{4}$$

$$Ce^{4+} + C_2O_4^{2-} \rightarrow C_2O_4^{-} + Ce^{3+} \tag{5}$$

$$Mn^{3+} + C_2O_4^{-} \rightarrow 2CO_2 + Mn^{2+} \tag{6}$$

$$Ce^{4+} + C_2O_4^{-} \rightarrow 2CO_2 + Ce^{3+} \tag{7}$$

Reaction (4) is much faster than (5); the greater activation energy for the sulfatocerate complex and oxalate ions than for the fairly unstable manganese(III) and oxalate ions may partly account for the observed rates. Electrostatic interaction indicates that electron transfer is more favorable with the positively charged manganese(III) than with the negatively charged sulfatocerate ions.

The rate of reaction (3) is not mentioned in the literature; however, the instantaneous appearance of the color of manganese(III) ions leads to the assumption that this reaction is comparatively faster than either (4) or (5). The color is especially prominent when a large excess of manganese(II) ions is present in the solution. The reaction rate is considerably hindered and the end-point becomes less sharp upon the addition of phosphoric acid or fluoride, which form stable complex ions with manganese(III) ions, thereby increasing the activation energy for reaction (4). In these cases, the manganese(III) color disappears slowly, and the results are somewhat low, since the rate of oxidation of low oxalate concentrations is slow enough to cause early end-points.

If proper precautions are taken, the proposed method has certain advantages over various existing methods. The operations are simple and no costly unstable catalysts are needed. Further, no indicators are required and the method is much superior to the simple visual titration of oxalate with cerium(IV) solutions, because of the increased reaction rate and the more contrasting color change from colorless or light pink to yellowish-brown or amber. Replicate determinations can be performed with a reproducibility within ±0.03 ml.

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A rapid method for the determination of polonium-210 and lead-210 in sea water

Polonium-210 and lead-210 in the natural environment have been the subject of much attention in recent years. Radon-222 escapes from the surface of the land into the atmosphere, where it decays via short-lived daughters to lead-210 and its daughters. Data for polonium-210 and lead-210 in the atmosphere and rains have been given by several authors[1-7]. Other authors have reported these nuclides in biological materials including foodstuffs, tobacco, blood, human and animal tissues and marine life[8-15].

Little work has been done on either polonium-210 or lead-210 in sea water. Lead-210 was first detected in sea water by RAMA *et al.*[16] and subsequently these findings were considered in more detail by GOLDBERG[17]. These observations were made on a small number of large sea water samples collected in the Eastern Pacific and the method employed involved coprecipitation of the lead followed by anion exchange and β-counting. The lead-210 content ranged from about 0.10 desintegrations $\min^{-1}\,l^{-1}$ in the upper water layers to 0.28 disintegrations $\min^{-1}\,l^{-1}$ at a depth of 2000 m. No values for the polonium-210 level in sea water seem to have appeared in scientific journals, although some data are given in two institutional reports[18,19]. FOLSOM[18] used iron(III) hydroxide as a scavenger on large sea water samples followed by α-counting and reported a mean polonium -210 value of 0.037 pCi l^{-1} (or 0.08 disintegrations $\min^{-1}\,l^{-1}$) for samples collected from Scripps Pier.

FLYNN[20] found that polonium is strongly adsorbed on to glass and, as it was evident from theoretical considerations that the polonium-210 content of sea water would be very small (*i.e.* at a level of 1 part in 10^{20} or 10^{21}), a cautious sampling and storage procedure was adopted.

Development

Polonium has been separated by solvent extraction techniques with various chelating agents such as thenoyltrifluoroacetone, or by extracting the ion-association complex with chloride into tributyl phosphate–dibutyl ether mixtures[21], but separation has usually been emphasized rather than concentration[22].

Since its synthesis by MALISSA AND SCHÖFFMANN[23], ammonium pyrrolidine dithiocarbamate (APDC) has been shown to form stable complexes with many elements over a wide pH range. Extraction of the APDC–metal chelates with 4-methyl-2-pentanone (methyl isobutyl ketone; MIBK) is a particularly useful technique, combining the benefits of rapid quantitative extraction over a wide pH range with minimum laboratory manipulation. The APDC–MIBK system has been extensively used as a pre-concentration technique in atomic absorption analysis[24] and quantitative recoveries of metals such as copper and zinc, present at parts per billion (10^9) levels in sea water, were obtained with a single 1-min extraction step by ORREN[25]. The chemistry of polonium resembles that of bismuth and lead more closely than that of the Group VI elements, and both bismuth and lead are extracted quantitatively with APDC–MIBK at pH 1–6[24]. Accordingly, this system was tested for extraction of polonium from sea water.

Extraction of polonium spikes with MIBK after addition of a 1%(w/v)APDC solution was incomplete at pH 2, but increasing the APDC concentration to 4%(w/v) increased the stability of the complex satisfactorily. The efficiency was further increased by a shaking period of 5 min rather than 1 min. MIBK is slightly soluble, and about 25 ml dissolves in a sample of 1.5 l of sea water. Experience with copper and zinc[25] indicated that all the chelate remained in the separated organic layer, despite lowered recovery of solvent, and this appears to be the case with polonium also. Standards were nevertheless run under the same conditions as samples to eliminate any possible error from this source.

Attempts to strip the organic layer with hydrochloric acid, in preparation for plating, failed because the acid and ketone phases did not separate (probably because of salt formation) and the solvent had to be evaporated off.

The method was subsequently found to be also suitable for lead-210. The whole procedure was carried out at a pH of 2 or lower to minimise possible adsorption problems.

Experimental

Reagents. All reagents were of analytical grade (BDH) except for the APDC (supplied by K and K Laboratories, New York) and the MIBK (BDH). Twice-distilled water from glass apparatus was used throughout.

Procedure. Collect 1.5-l sea water samples at predetermined depths by means of a suitable, cleaned, plastic sampler. Immediately run the samples into volumetrically calibrated polythene bottles (which have been previously rinsed with hydrochloric acid and then with distilled water) containing 30 ml of 11.7 *M* hydrochloric acid. Freeze rapidly and store the samples at −20° until they are to be analyzed.

Thaw the samples rapidly before analysis, and transfer them to glass beakers. Carefully adjust the pH to 2.0 by the addition of ammonia solution. Transfer the solution immediately to a 2-l separating funnel and add 15 ml of freshly prepared 4%(w/v)APDC solution. Shake the funnel vigorously for 1 min, allow to stand for 5 min and then shake again for 1 min. Add 75 ml of solvent (MIBK) and shake the contents for 5 min, after which leave to separate out for 30 min. Discard the aqueous portion and add 6 ml of 11.7 *M* hydrochloric acid to the organic extract. After shaking, transfer the acid and organic layer to a glass beaker and evaporate nearly to dryness (*i.e.*, to about 0.5 ml) on a hotplate (b.p. of MIBK is 114°–117°).

Dissolve the residue in 10 ml of 11.7 *M* hydrochloric acid. Plate the polonium-210 out of the acidic solution using the deposition cell and the chemical technique of FLYNN[20], but substitute teflon for perspex, which is attacked by MIBK in the plating solution.

After the first plating, retain the plating solution and store for two or more months in polythene bottles after which time again plate out. By allowing any lead-supported polonium-210 to build up, an estimate of the lead content can be made[8,14,15]. Statistics are considerably improved if samples are stored for four months between platings instead of for two months.

Pack the silver discs on a zinc sulphide phosphor as described previously[12,13,26], the only difference being that the silver disc forms the material to be counted. This provides an individual sealed sample phosphor system, thereby minimising the likelihood of contamination. Count samples on a conventional photomultiplier assembly.

Obtain the background blank for the technique by performing the entire solvent extraction and plating on a doubly distilled water sample.

Confirm that all the counts above background are in fact due to polonium-210 only, by subsequent counting of the silver discs on a multi-channel α-spectroscopy semi-conductor detector system.

Discussion and results

The efficiency of the solvent extraction method for polonium-210 was determined by the addition of lead-210 plus polonium-210 (in equilibrium) spikes ranging from 0.04 to 600 pCi l^{-1}. A linear calibration curve was obtained and the overall efficiency of the entire extraction and plating technique was 92%. Similarly, an overall efficiency of 85% was obtained for the lead-210 determinations. The background/reagent blank gave a count-rate of 1.00 ± 0.05 counts h^{-1}.

The sea water samples were collected at a standard depth of 20 m at stations on separate cruises by R.S. Africana II and R.S. Sardinops during March 1969. This depth was chosen as representative of the upper mixed layer and at the same time free of possible contamination from the ship. All data were corrected for unsupported polonium-210 decay and supported polonium-210 build-up and are expressed as activities at time of collection. In the calculations the half-lives of lead-210 and polonium-210 were taken as 21.4 years and 138 days, respectively.

The mean polonium-210 and lead-210 concentrations in surface sea water around South Africa during March 1969 were about $20(\pm 3) \cdot 10^{-15}$ Ci l^{-1} (0.44 disintegrations $min^{-1}\,l^{-1}$) and about $38\,(\pm 10) \cdot 10^{-15}$ Ci l^{-1} (0.084 disintegrations $min^{-1}\,l^{-1}$), respectively. The errors given are the standard deviations caused by counting statistics only. The full results and their detailed interpretation will be described elsewhere[27].

Conclusions

The levels of polonium-210 and lead-210 can conveniently be measured in small sea water samples by solvent extraction followed by α-counting and/or α-spectrometry. Although 1.5-l samples are adequate for polonium-210 measurements, larger samples would be more satisfactory for lead-210 determinations.

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Determination of naphthacene traces by sensitized luminescence on filter paper

The sensitized luminescence of naphthacene in anthracene crystals has been known for a long time. The observations of BOWEN *et al.*[1] and GANGULY[2] proved that pure crystalline naphthacene hardly shows luminescence when excited by ultraviolet radiation. However, if the anthracene crystal lattice contains a naphthacene contamination of the order of 10^{-8}–10^{-4} mole per mole, the anthracene emission considerably decreases, and an intense yellow-green fluorescence appears[3,4]. The quantitative interpretation of the energy transfer mechanism of the excitation energy has been elaborated by FÖRSTER[5] and BIRKS[6].

The sensitized luminescence of naphthacene does not appear to have been applied analytically. The aim of the work described here was to determine traces of naphthacene on filter paper. For this purpose, the intensity ratio of the anthracene and naphthacene luminescence measured at certain characteristic luminescence maxima was used.

Experimental

The fluorescence intensities were measured with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. A sample holder suitable for measuring the luminescence of solid materials such as paper and powder was specially designed (Fig. 1). The sample forms an angle of 45° with the excitation beam.

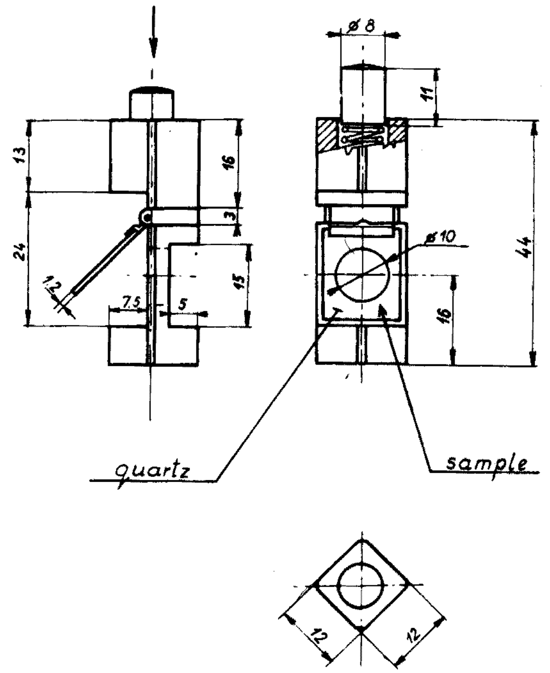

Fig. 1. Sample holder for measuring the luminescence of solids.

For the investigations, p.a. anthracene, naphthacene and benzene were used. Preliminary tests showed that the anthracene and benzene were free of even traces of naphthacene. For preparing the samples, benzene solutions of anthracene and naphthacene were used. The solutions contained $3 \cdot 10^{-3}$ *M* anthracene and $5 \cdot 10^{-5}$–10^{-11} *M* naphthacene. After Whatman No. 1 paper slides had been immersed in the solution, the samples were dried in air at room temperature for about 60 min. The paper samples were then placed into the sample holder and irradiated at 370 nm, which wavelength is near one of the active absorption maxima of the anthracene. Fluorescence was measured at the anthracene emission peak at 420 nm (I_{420}) and at the naphthacene emission peak at 497 nm (I_{497}). For evaluation, no correction of the spectra was needed.

Results and discussion

The fluorescence spectrum of the system changes considerably when the amount of naphthacene is increased; details have been given by PARKER[3]. At ultratrace levels of naphthacene, the 495–497-nm naphthacene band is suppressed by the emission of anthracene. The optimal amount of anthracene proved to be about 10^{-3} *M*.

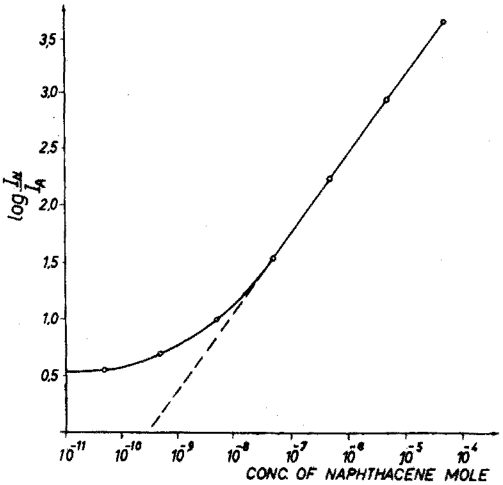

Fig. 2. Intensity ratio of the fluorescence of anthracene crystals containing naphthacene *vs.* naphthacene concentration. I_N = naphthacene intensity at 497 nm; I_A = anthracene intensity at 420 nm.

In the naphthacene concentration range of 10^{-8} M–$5 \cdot 10^{-5}$ M, the I_{497}/I_{420} factor is linear (Fig. 2). For smaller concentrations, the curve deviates from the linear, but emission can be measured for as little as $5 \cdot 10^{-11}$ M naphthacene. This range can be reproduced reliably, and is therefore suitable for quantitative work after suitable calibration. The deviation from the linearity is most probably due to the fact that in this range of concentration the anthracene emission as well as other energy-transfer processes interfere to some extent.

The relative error of measurements in the range $5 \cdot 10^{-5}$–10^{-8} M increases from 0.5–1.0% to 8–10%. The amount of naphthacene calculated for the Whatman No. 1 paper prepared from 10^{-11} M solution is of the order of 10^{-14} g. Under the above conditions this quantity can be measured with good reliability.

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BOOK REVIEWS

LOTHAR SACHS, *Statistische Auswertungsmethoden*, Zweite, neubearbeitete und erweiterte Auflage, Springer Verlag, Berlin, 1969, xxx+677 pp., Price: Bound DM 58,—; $14.50.

This detailed book on statistical methods has been written for a wide audience ranging from scientists through engineers and medical workers to economists. The text is arranged into 7 chapters, preceded by an introductory one (marked as Chapter 0), in which all the non-statistical mathematical operations necessary to understand the later parts are described. Chapter 1 on Statistical Tests includes all the mathematical statistics used in the book, plus the theoretical treatment of statistical testing. This is followed by a practical chapter where the application of simple tests in medicine and industry is described. Two chapters deal with the statistics of data which are independent from one another; which of course include results of parallel measurements. Chapter 5, on the other hand, deals with correlation and regression (that is on data which are dependent on one another); the analytical chemist, who uses calibration graphs based on the measurement of individual points, will find this part useful. A chapter on three- and four-dimensional statistics is followed by another on the analysis of variance. A very detailed bibliographic section (running to 90 pages), calculation exercises and their solution, a short German–English dictionary (1 page only) and an Index are also enclosed.

In many ways the book provides too much material for an analytical chemist, who needs to find his way first among the vast amount of information which is included. Many of the examples, taken mainly from the medical aspect, are irrelevant for the chemist, while some others have to be fully understood before their application to analytical problems could be attempted. But the statistically minded chemist, who has other introductory texts at his disposal, will find this book useful, primarily because of the clear presentation of the material, detailed statistical tables, well described mathematical operations and comprehensive bibliography.

G. SVEHLA, Belfast

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Short Communications

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