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Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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ANALYTICA CHIMICA ACTA

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Papers will be published in English, French or German.

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Papers should be sent to: Prof. Philip W. West, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.)
or to
Dr. A. M. G. Macdonald, Department of Chemistry, The University, P.O. Box 363, Birmingham 15 (Great Britain)

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Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (*e.g.*, 2%, 2 ml, 2 g, 2 μl, 2 μg, 2 ng, 2 cm, 200 mμ).

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1. J. J. Lingane and A. M. Hartley, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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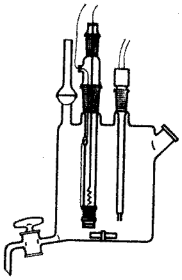
Ensemble de coulométrie automatique de Jean BIZOT

Monsieur BIZOT a présenté à la Société Chimique de France, le 23 avril 1965, une nouvelle méthode de dosage de petites quantités d'eau. Elle est décrite dans la publication suivante:
J. BIZOT - Méthode automatique de dosage coulométrique de petites quantités d'eau. Bull. Soc. Chim. France janvier 1967, page 151.



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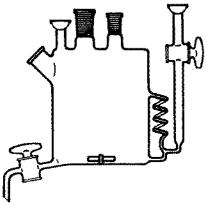

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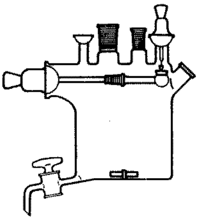

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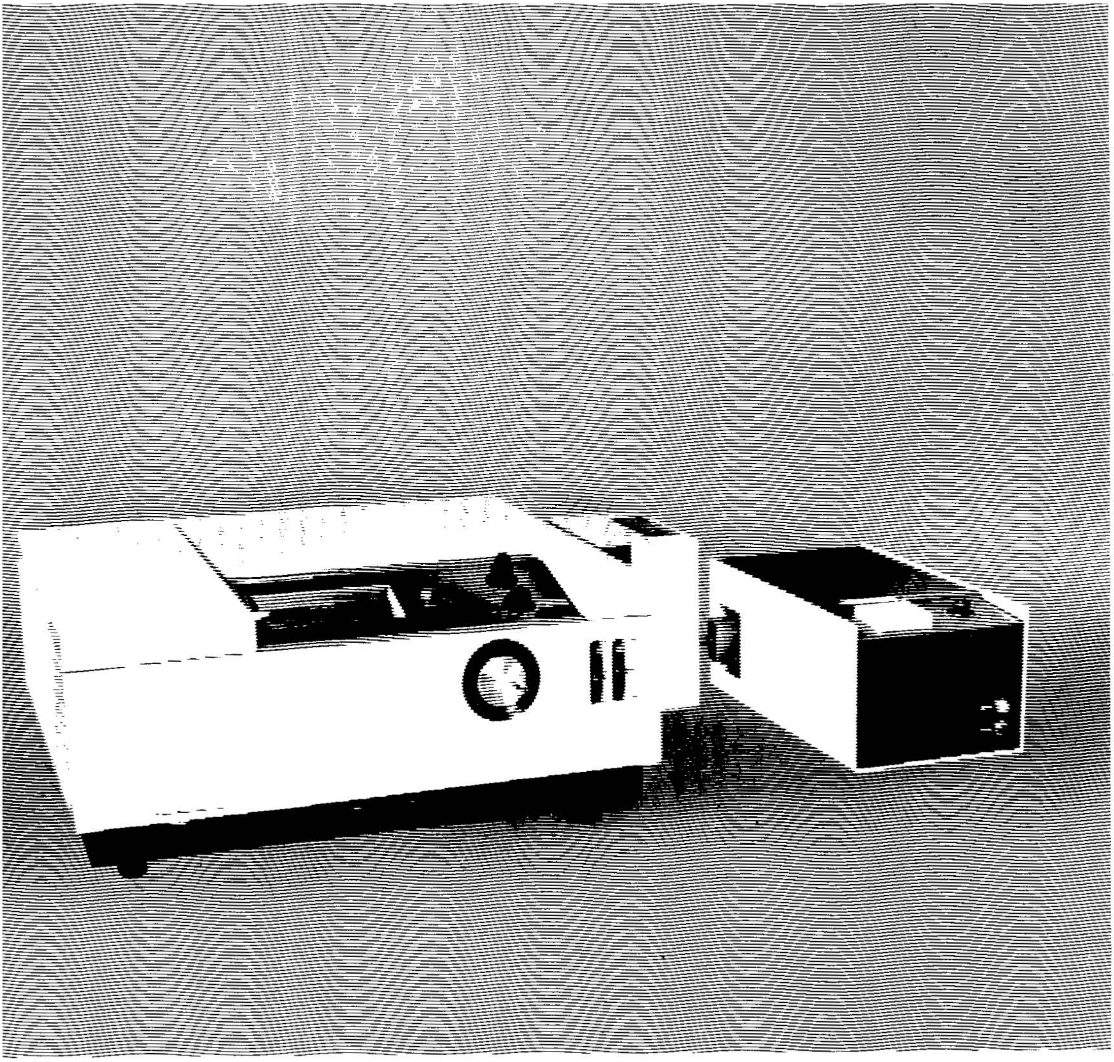

X-RAY EMISSION SPECTROGRAPHY IN GEOLOGY

Methods in Geochemistry and Geophysics, 4

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

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

X-ray emission analysis (fluorescence and electron probe) has become an extremely powerful analytical technique for the geochemist. It is important that its principles should be clearly stated if full advantage is to be taken of the technique.
This book is written with the earth scientist in mind and throughout emphasizes the power of the method to supply meaningful chemical information about geological samples.

Contents: Preface. Introduction. The origin and nature of X-rays. Excitation. Detectors and electronics. Dispersion and geometry. Analysis (qualitative and semi-quantitative). Quantitative analysis. Principles of X-ray microanalysis with the electron probe. Instrumentation. Procedures for quantitative electron-probe microanalysis. Applications of the electron-probe X-ray microanalyzer in mineralogy. Appendix. References. Index.

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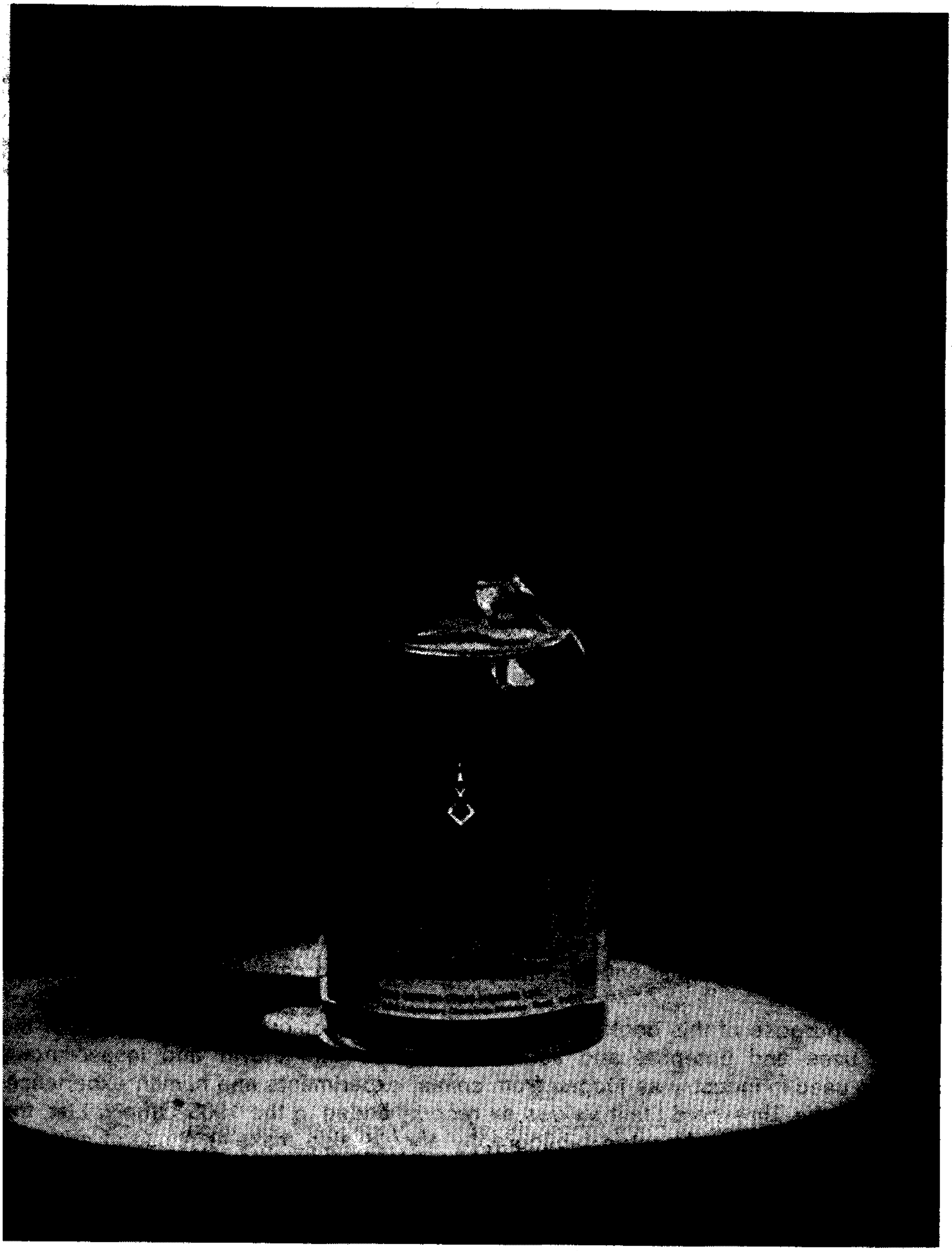

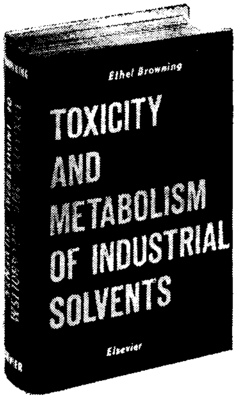

TOXICITY AND METABOLISM OF INDUSTRIAL SOLVENTS

by ETHEL BROWNING,
M. D., formerly H. M. Medical Inspector of Factories,
Ministry of Labour and National Service, London

7 x 10", xi + 739 pages, 4 tables, 1922 lit. refs.,
1965, £ 9.10.0, Dfl. 95.00 or $ 32.50

Since the publication of the second edition of The Toxicity of Industrial Organic Solvents in 1953, under the auspices of the Medical Research Council of Great Britain, many new solvents have come into world-wide use, and many new investigations of their toxic effects have been made. It was therefore thought advisable to make a new assessment of this mass of new data.

With the permission of the Medical Research Council, the original publication (now out of print) has formed the basis of the present volume. But this is by no means merely a revised edition; it is, as agreed with the M.R.C., an entirely new book with an entirely new title. The introduction of the word metabolism in the new section headings draws attention to the importance of this aspect of the subject, since it is now universally recognised that the toxic effects of certain chemical substances depend almost entirely on their fate in the organism under the influence of enzymes.

The main purpose of this book is to make available a comprehensive account of the nature, uses and potential and actual toxicity of well-known and lesser-known solvents used in industry as judged from animal experiments and human experience. Recording the Threshold Limit Values as recommended in the 1965 Official List, the detailed and fully documented bibliography should also make it a useful adjunctn to reference libraries.

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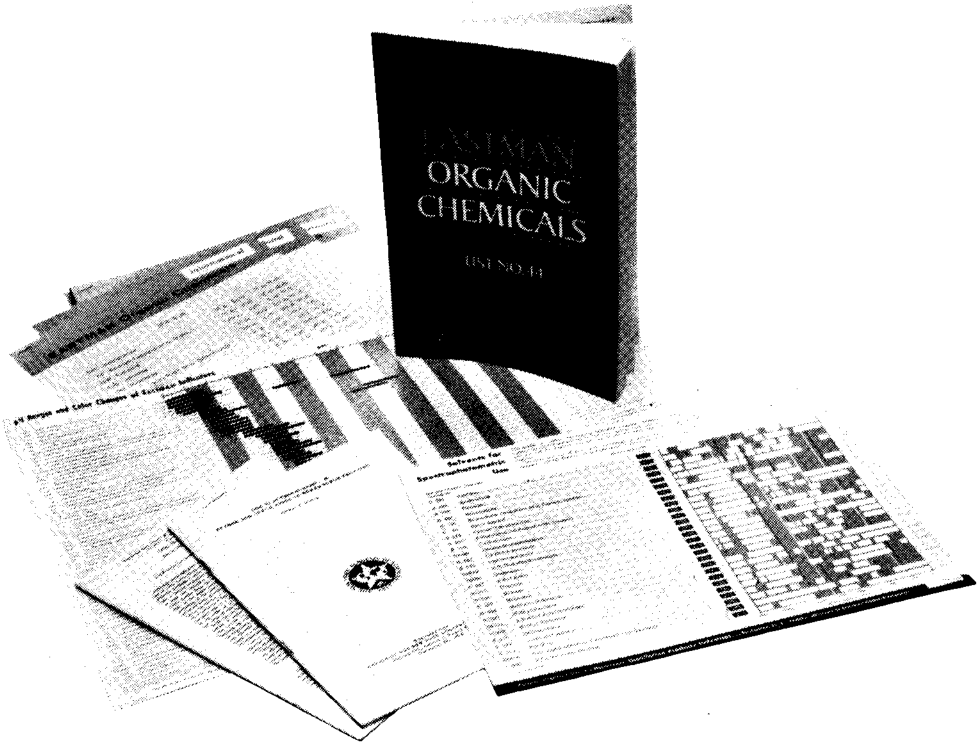
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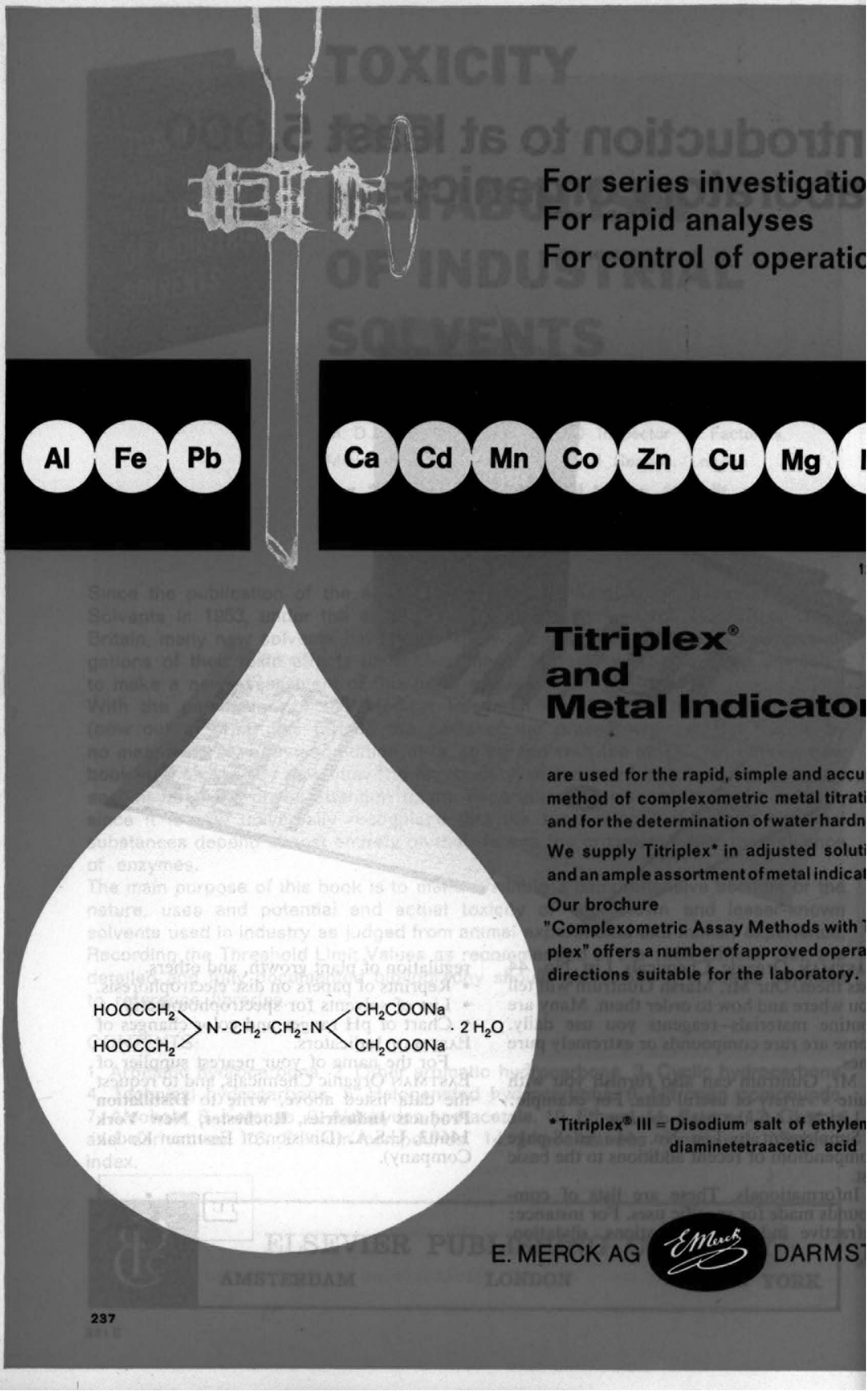

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 39, No. 2, October 1967

PURIFICATION OF PYRIDINE FOR VOLTAMMETRIC STUDIES

EFFECT OF IMPURITIES

Purification of pyridine by zone fractional crystallization reduces the concentration of prewave-producing contaminant below polarographic detection limits, *i.e.*, 0.01 mM. A qualitative test based on the stability of the free radical diphenylpicrylhydrazyl has shown the method to be capable of reducing the concentration of proton-releasing impurities. Water is also removed. Investigation of the effect of the contaminants in normal reagent-grade pyridine on the electrocapillary curves and polarograms of pyridine solutions containing lithium perchlorate and tetraethylammonium perchlorate as background electrolytes in the presence and absence of oxygen, has indicated that the impurities are capable of changing the mechanism for the electrochemical reduction of oxygen in pyridine.

D. A. HALL AND P. J. ELVING,
Anal. Chim. Acta, 39 (1967) 141–149

THE APPLICATION OF SUBSTOICHIOMETRIC RADIOISOTOPIC DILUTION PRINCIPLES TO CONTROLLED-POTENTIAL COULOMETRY AND SOLVENT EXTRACTION

Radioisotope dilution principles are applied to controlled-potential electrolysis and solvent extraction with dithizone for the determination of trace amounts of cadmium. A method was developed to verify whether or not the substoichiometric principle was obeyed. If the substoichiometric principle was not obeyed, analysis was still possible by means of calibration curves. In order to obtain independent verification of the series controlled-potential method and to establish a means of comparison with the radioisotope dilution technique a current integration procedure was also employed. A microtechnique was used to extend the sensitivity of the solvent extraction system for cadmium. Standard zinc spelter and high-purity zinc were analyzed for cadmium after separation by a method of standard addition.

A. R. LANDGREBE, L. T. MCCLENDON, J. R. DEVOE, P. A. PELLA AND W. C. PURDY,
Anal. Chim. Acta, 39 (1967) 151–159

LINE SOURCES IN ABSORPTION SPECTROSCOPY

Hollow-cathode tubes and discharge lamps are studied as spectral sources for absorption spectrophotometry. Comparisons are made of monochromatic *versus* conventional continuous sources with respect to several experimental parameters, particularly the effect of slitwidth. Working curves are shown to indicate the possible advantages of using line sources for narrow band absorption systems.

W. W. HARRISON AND K. CAUFIELD,
Anal. Chim. Acta, 39 (1967) 161–166

TITRATION CURVES OF COMPLEXIMETRIC TITRATIONS OF MIXTURES OF METAL IONS WITH ONE LIGAND

PART I. MATHEMATICAL EXPRESSIONS

Formulae were calculated for the compleximetric titration of mixtures of two and of three metals with one ligand, giving the relation between a titration parameter f and the concentration of the metals, the ligand or the complexes separately.

U. HANNEMA AND G. DEN BOEF,
Anal. Chim. Acta, 39 (1967) 167–173

THE NEPHELOMETRIC DETERMINATION OF SMALL AMOUNTS OF SULPHATE ION

A method is proposed for the nephelometric determination of the sulphate ion in concentrations of 2.5–25 p.p.m. in test volumes of 10 ml. The sulphate is precipitated with a solution of 4-amino-4′-chlorodiphenyl hydrochloride, and the resultant suspension of amine sulphate is stabilised with gum ghatti. Phosphate ions interfere and are removed as magnesium ammonium phosphate beforehand. Fluoride ion up to 25 p.p.m. has no effect on the determination.

J. M. MARTIN AND W. I. STEPHEN,
Anal. Chim. Acta, 39 (1967) 175–180

THERMOMETRIC STUDIES OF COMPLEX FORMATION WITH IRON(III), ALUMINIUM AND GALLIUM

PART I. OXALATES AND MALONATES

(in French)

Apparatus and experimental techniques are described for the thermometric detection of the stepwise formation of trivalent cation complexes with oxalate and malonate anions. The three iron and aluminium malonates were confirmed by this method but only two of the three oxalates could be found.

J.-P. GALLET AND R. A. PÂRIS,
Anal. Chim. Acta, 39 (1967) 181–188

THE REACTION BETWEEN PALLADIUM(II) AND COMPLEXES OF 8-QUINOLINOL-5-SULFONIC ACID

Anomalous results for the reaction between palladium(II) and fluorescent complexes of 8-quinolinol-5-sulfonic acid were found to be due to a slow reaction. Heating the solution permits the determination of palladium(II) in combination with copper(II) or nickel(II), the two cations being titrated stepwise. The approximate value for the overall formation constant of the PdL_2^{2-} complex was determined.

J. A. BISHOP,
Anal. Chim. Acta, 39 (1967) 189–194

THE DETERMINATION OF ALKALI AND ALKALINE EARTH METALS BY PRECIPITATION TITRATION IN NON-AQUEOUS MEDIA

(in German)

Precipitation titrations of the cations of salts such as sodium perchlorate, potassium hexafluoroarsenate, barium perchlorate and barium iodide, were investigated in acetone and methyl isobutyl ketone media. The titrant was a solution of lithium chloride in the same ketone and end-points were detected oscillometrically or conductometrically. The different types of titration curve found can be explained by comparing the specific conductivities of the solutions before and after titration. Barium iodide and barium perchlorate can be determined in both ketones with an error of ±1%. In the case of sodium perchlorate and potassium hexafluoroarsenate, accurate titrations are possible only in methyl isobutyl ketone media.

G. HENRION AND E. PUNGOR,
Anal. Chim. Acta, 39 (1967) 195–202

A COMPARISON OF ELECTROMETRIC AND GASOMETRIC METHODS FOR FOLLOWING AUTOXIDATIONS

Gasometric and electrometric methods for determining oxygen in the study of photosensitized reactions are compared. The oxygen electrode must be calibrated against known solutions similar in composition to the solutions used in the reactions that are studied. The electrode can be used to study initial reaction rates whereas this is impossible for fast reactions with the Warburg apparatus.

J. S. Bellin and C. A. Yankus,
Anal. Chim. Acta, 39 (1967) 203–208

LIQUID EXTRACTION OF MOLYBDOPHOSPHORIC AND MOLYBDOARSENIC ACIDS: APPLICATION TO THE DETERMINATION OF PHOSPHORUS IN THE PRESENCE OF ARSENIC

The radioisotopes phosphorus-32 and arsenic-74 have been used to study the extraction of molybdophosphoric and molybdoarsenic acids from aqueous solution with various organic solvents. A method is described for the gravimetric determination of phosphorus in the presence of arsenic which makes use of solvent extraction with *n*-butyl acetate. The results obtained for the determination of phosphorus in various types of iron and steel are described.

R. B. Heslop and E. F. Pearson,
Anal. Chim. Acta, 39 (1967) 209–221

CHEMICAL DETERMINATION OF SOME MAJOR CONSTITUENTS IN ROCKS AND MINERALS

Macro-analytical schemes are described for the determination of aluminium, total iron and iron(II), as part of the complete analysis of silicate rocks and minerals. Solvent extraction eliminates interferences before titration of aluminium with DCTA. Iron(III) is extracted with MIBK and determined indirectly with EDTA. Iron(II) is determined by potentiometric titration under an inert atmosphere. Interferences are removed with 2,4-pentanedione and carbon tetrachloride before the determination of calcium and magnesium.

E. Kiss,
Anal. Chim. Acta, 39 (1967) 223–234

A CATALYTIC METHOD FOR THE DETERMINATION OF NICKEL

The catalytic effect of nickel on the decomposition of permanganate in alkaline solution in the presence of acetodiphosphonic acid is used as a basis for a method for the determination of 0.1–0.7 p.p.m. of nickel. A solvent extraction procedure eliminates the interferences of silver, cobalt, copper and iron, and can be used to concentrate lower concentrations of nickel.

D. Mealor and A. Townshend,
Anal. Chim. Acta, 39 (1967) 235–244

UTILIZATION OF ULTRACENTRIFUGATION FOR MASS MEASUREMENT AND IN STUDIES OF POLYDISPERSITY IN SYNTHETIC POLYMERS

(in French)

After a review of the two techniques based on sedimentation rate and equilibrium in binary medium, more recent methods involving the presence of a second non-macromolecular solute are described. Application of these methods to synthetic polymers is still rare but of increasing interest. The use of computers simplifies the exploitation of the measurements.

H. Benoit and M. Jacob,
Anal. Chim. Acta, 39 (1967) 245–257

SPECTROPHOTOMETRIC DETERMINATION OF SOME ALDEHYDES AND KETONES WITH 2,4-DINITROPHENYLHYDRAZINE

(Short Communication)

R. N. Heistand,
Anal. Chim. Acta, 39 (1967) 258–260

THE USE OF MERCURY(II) BROMIDE AS COATING IN A PIEZOELECTRIC CRYSTAL DETECTOR

(Short Communication)

G. G. Guilbault,
Anal. Chim. Acta, 39 (1967) 260–264

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH ISONITROSOACETOPHENONE

(Short Communication)

(Kum) U. B. Talwar and B. C. Haldar,
Anal. Chim. Acta, 39 (1967) 264–267

A RAPID EMPIRICAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF HYDROXYL AND ALUMINIUM IN ALUMINATE AND BASIC ALUMINIUM NITRATE SOLUTIONS

(Short Communication)

H. H. Ph. Moeken and W. A. H. Van Neste,
Anal. Chim. Acta, 39 (1967) 267–269

INTERFERENCE FROM NATURAL RADIOACTIVITY IN NEUTRON ACTIVATION ANALYSIS FOR BISMUTH IN LEAD

(Short Communication)

R. De Boeck, F. Adams and J. Hoste,
Anal. Chim. Acta, 39 (1967) 270–272

EFFECT OF AMINES ON ATOMIC ABSORPTION ANALYSES

F. R. Hartlage, Jr.,
Anal. Chim. Acta, 39 (1967) 273–275

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PURIFICATION OF PYRIDINE FOR VOLTAMMETRIC STUDIES

EFFECT OF IMPURITIES

DAVID A. HALL AND PHILIP J. ELVING
The University of Michigan, Ann Arbor, Mich. (U.S.A.)
(Received March 28th, 1967)

The importance of the degree of purity of a solvent used as a medium for voltammetric studies cannot be overemphasized. Solvents commonly used in nonaqueous voltammetry such as acetonitrile, dimethylformamide, dimethylsulfoxide and pyridine are received from the manufacturer with questionable degrees of purity with respect both to their water content and to other contaminants specific to the particular solvent. Some of these contaminants may have adverse effects on the electrolytic behaviour of the compounds studied in them, *e.g.*, intermediates, such as free radicals, may be destroyed without detection, extra waves may appear, wave patterns may be distorted, and control of proton concentration, so important in the study of organic compounds, may be impossible.

Various more or less effective means of purification have been reported for specific solvents, *e.g.*, ref. 1. In some cases, impurities have been detected, their voltammetric characteristics described, and, because of lack of an adequate means of purification, the solvents have been prudently used; pyridine is an example[2–5].

A small prewave to the pyridinium ion reduction in pyridine has been related to a predischarge wave present in the absence of protons; the sum of the two wave-heights is constant[2]. The magnitude of the prewave varies with the brand of pyridine and even with different lots of the same brand. Contrary to what one might assume, presumably better quality spectral-grade samples of pyridine show, in some cases, a higher prewave than ordinary reagent-grade solvents.

Since the detection of the prewave and the postulation of its origin in impurities, the authors' laboratory has embarked on a concerted effort to remove and, if possible, to identify the impurities. Many means of purification, such as that mentioned[6] for the purification of pyridine for nonaqueous titrations, have been tried; these methods, although quite effective in removal of water and active proton-containing compounds, leave the prewave material untouched. However, a successful means of purification has been developed, although the impurities have not yet been satisfactorily identified owing to their very low concentration in pyridine, *e.g.*, 0.2 m*M*.

The method of purification, which can be described as zone fractional crystallization, is capable of reducing the concentration of prewave-producing material below the detection limits of polarography, *i.e.*, 0.01 m*M*. Water and other impurities are also removed. Comparison of the electrocapillary curves observed in the presence and absence of oxygen in pyridine in various stages of purification containing two different background electrolytes has revealed important effects due to the impurities. Since the stability of the diphenylpicrylhydrazyl free radical was found to be dependent on the concentration of proton-releasing impurities present, this phenomenon can be used as an index of the purity of the pyridine.

EXPERIMENTAL

Reagents

The pyridine used was a composite of Baker & Adamson reagent grade (Lot No. Z144) and J. T. Baker analyzed reagent grade (Lot No. 37529); the mixture contained a concentration of impurity which is the average of that found in many brands and lots. The Baker & Adamson pyridine was rich in the prewave-producing material; the J. T. Baker pyridine, which was free of the impurity, was used as a diluent. Lithium perchlorate (G. Frederick Smith Chemical Co. anhydrous grade) was dried at 110° for 2 h. Tetraethylammonium perchlorate (Eastman) was vacuum-dried at room temperature. Nitrogen, which had been passed through anhydrous calcium sulfate, was used to provide a dry inert atmosphere above the freezing solvent and the melting solid. Argon was similarly dried.

Apparatus

The fractional crystallization apparatus consisted of a glass freezing tube (14-in long; 2-in diameter) provided with a polyethylene cap having a nitrogen inlet and an entrance for the stirrer blade, which was a one-turn screw type blade (0.75-in wide; 1-in long), driven by a 1200-rev./min motor.

Polarograms were recorded by means of a Sargent Model XV Polarograph in conjunction with a Sargent Model A IR Compensator. The Sargent Model XV was used as a potential source for electrocapillary curve measurement.

The D.M.E. capillary, made from marine barometer tubing, had an $m^{2/3}t^{1/6}$ product in 0.1 *M* $LiClO_4$ in oxygen-free pyridine at open circuit of 1.467 ($t = 4.18$ sec; $m = 1.12$ mg/sec). Two jacketed three-compartment cells were used. One cell used only for pyridine solutions of Et_4NClO_4 had a platinum spiral counter electrode in one end compartment and a normal silver electrode (NAgE) in pyridine[7] in the other. Sintered glass disks and gel salt bridges (0.1 *M* Et_4NClO_4 in pyridine plus 7.5% by weight of methyl cellulose) separated the compartments; 0.1 *M* Et_4NClO_4 was present in the reference and counter electrode compartments. The second cell, which was used only for pyridine solutions of $LiClO_4$, was the same as the first except that the gel salt bridges consisted of 0.8 *M* $LiClO_4$ in pyridine plus 10% by weight of methyl cellulose and 0.1 *M* $LiClO_4$ was present in the reference and counter electrode compartments.

All potentials reported are *versus* the NAgE at 25°.

Fractional crystallization procedure

The freezing tube containing 500 ml of reagent-grade pyridine was so mounted that the blade of the stirrer was at half the total depth of the pyridine. The polyethylene cap was placed in position and the dry nitrogen stream turned on to displace air from the tube. The stirring motor was then turned to its maximum speed and a Dry Ice–2-propanol bath at −75° was brought into position such that the lower 2 inches of the freezing tube were immersed in the bath. Sufficient time was allowed for crystal formation at the bottom of the freezing tube; then, the bath was lowered and the crystals allowed to melt until only a few remained on the bottom of the tube; the depth of immersion of the tube in the bath was then increased *ca.* 1.5 inches at a time, allowing crystal formation at each stage until the top of the bath was at a level about 1 inch above the stirrer blade. The time necessary was *ca.* 2 h, by which time about 50% of the pyridine was frozen. The stirrer was then stopped, the bath lowered, the liquid fraction decanted, the tube was re-capped, and the solid fraction allowed to melt in a stream of dry nitrogen. The zone fractional crystallization was then repeated on the liquified solid fraction.

Polarograms were taken of 0.1 *M* $LiClO_4$ solutions in the pyridine fractions obtained in each stage of the purification process.

Electrocapillary curve procedure

The electrocapillary curves were taken at 25°±0.2°; drop-time was measured at 100-mV intervals between 0.0 V and the cathodic background electrolyte discharge. Solutions containing oxygen were air-saturated; those which did not contain oxygen, were deaerated by a 20-min purge with dried argon. Curves were taken on the composite reagent-grade pyridine, the liquid fraction of the first fractionation, and the solid fraction of the second fractionation. Polarograms of these samples, which contained a suitable electrolyte, were recorded before and after the electrocapillary data had been taken.

ZONE FRACTIONAL CRYSTALLIZATION

The results of purification of pyridine shown in Table I are based on several purification experiments and on a postulated concentration of predischarge wave-producing material of 0.02 g per liter of pyridine, which corresponds to a 0.2 m*M* concentration of a substance with a molecular weight of 100. The figure of 0.2 m*M* is based on the average of the prewaves for a large number of pyridine samples, as-

TABLE I

POLAROGRAPHIC EVALUATION OF THE PURIFICATION OF PYRIDINE BY ZONE FRACTIONAL CRYSTALLIZATION

Pyridine used	*Volume (ml)*	*Predischarge wave*[a]		*Impurity*[b]	
		$E_{1/2}$ (*V*)	i_l (*μA*)	m*M*	*g*
Composite Reagent Grade	1000	−1.72	0.78	0.200	0.020
First fractionation:					
Liquid fractn.	585	−1.72	1.27	0.323	0.019
Solid fractn.	415[c]	−1.71	0.09	0.024	0.001
Second fractionation:					
Liquid fractn.	130	−1.72	0.23	0.059	0.0008
Solid fractn.	225	Not detectable			

[a] In 0.1 *M* $LiClO_4$ solution.
[b] Weight based on 0.02 g/1000 ml as discussed in text.
[c] 60-ml sample removed for polarographic evaluation of predischarge wave.

suming a 1-electron process[2]. Polarograms of 0.1 M $LiClO_4$ solutions of the starting material and two fractions are shown in Fig. 1.

A material balance for the predischarge wave material for the first fractionation, based on the measured currents, shows a total weight of 0.0199 g, compared to the hypothetical starting weight of 0.0200 g. The efficiency of the first fractionation was 88%, defined as follows:

$$\%E = \frac{(\text{wt. } X/\text{ml original pyridine}) - (\text{wt. } X/\text{ml 1st solid fraction})}{\text{wt. } X/\text{ml original pyridine}} \cdot 100$$

The efficiency of the second fractionation was 78%. The yield of purified pyridine, based on the original volume of pyridine, was 27%.

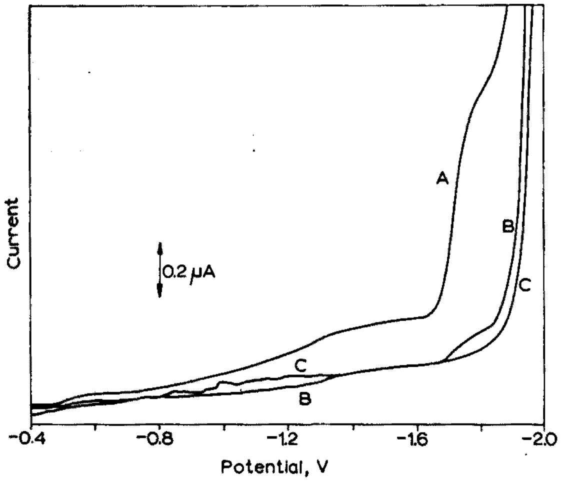

Fig. 1. Effect of zone fractional crystallization on the magnitude of the predischarge wave in a 0.1 M $LiClO_4$ in pyridine solution. (A) Composite reagent-grade pyridine. (B) First solid fraction obtained. (C) Second solid fraction obtained.

EFFECT OF PURIFICATION ON ELECTROCAPILLARY BEHAVIOR

Electrocapillary curves of 0.1 M $LiClO_4$ and 0.046 M Et_4NClO_4 solutions in pyridine obtained from different purification stages were measured in the absence and presence of oxygen. In the subsequent discussion, "purified pyridine" refers to the second solid fraction obtained in the crystallization and "impure pyridine" to the first liquid fraction.

Lithium solutions

The electrocapillary maximum in 0.1 M $LiClO_4$ in purified pyridine is at −0.40V.

The concentration of impurities significantly affects the electrocapillary curves in both the presence and absence of oxygen. Figures 2 and 3 show the relevant electrocapillary curves; the depth of the indentation at −0.40 V in the presence of oxygen, which is probably the most striking characteristic of the electrocapillary curves, markedly increases with increasing purity; this potential is located at the foot of the first reduction wave of oxygen. Such a decrease in drop-time may be attributed to adsorption of oxygen on the surface of the mercury drop[8], since no such decrease in drop-time is seen at −0.40 V in the absence of oxygen.

Associated with increase in impurity is a decrease in magnitude of the apparent maximum on the first oxygen reduction wave at −0.60 V and a shift of the second

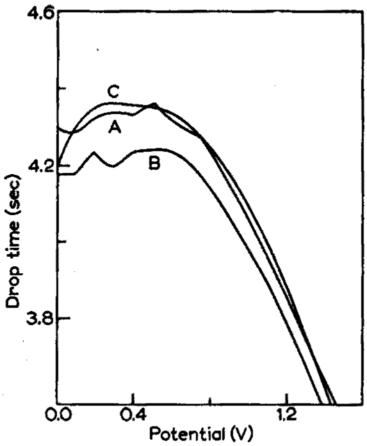

Fig. 2. Electrocapillary curves of 0.1 M $LiClO_4$ solution in various grades of pyridine in the absence of oxygen. (A) Pyridine from the second solid fraction of zone fractional crystallization. (B) Composite reagent-grade pyridine. (C) Pyridine from the first liquid fraction of zone fractional crystallization.

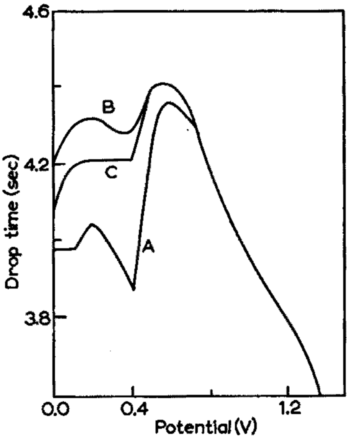

Fig. 3. Electrocapillary curves of air-saturated 0.1 *M* $LiClO_4$ solutions in various grades of pyridine. A, B and C: as in Fig. 2.

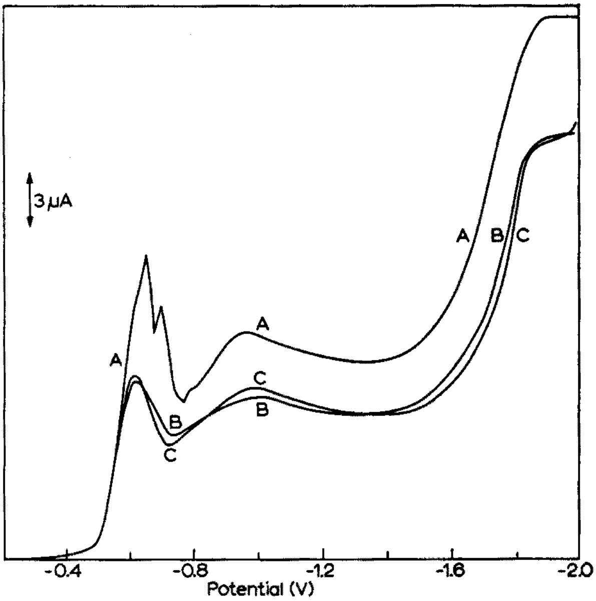

Fig. 4. Polarograms of air-saturated 0.1 *M* $LiClO_4$ solutions in various grades of pyridine. A, B and C: as in Fig. 2.

reduction wave half-wave potential to more positive values (Fig. 4; Table II). The peaking is believed to be due to formation of a film by the product of the first oxygen reduction; the film acts as an insulator to further current passage. This assumption is supported by the fact that the current reaches its maximum value at about half of the drop growth and approaches a minimum as the mercury drop reaches its maximum size. The current reversal phenomenon occurs between −0.60 and −0.70 V and persists until a potential of *ca.* −1.80 V is reached, when the film is reduced.

TABLE II

EFFECT OF IMPURITIES ON THE POLAROGRAPHIC BEHAVIOR OF OXYGEN IN PYRIDINE

Pyridine	*Wave*	*0.1 M $LiClO_4$ solution*				*0.046 M Et_4NClO_4 solution*			
		$E_{1/2}$ (*V*)	i_1 (*μA*)	i_I/i_{II}	*Slope*[a] (*mV*)	$E_{1/2}$ (*V*)	i_1 (*μA*)	i_I/i_{II}	*Slope*[a] (*mV*)
Composite Reagent Grade	I	−0.55	13.76	4.1	42	−0.94	9.45	1.2	69
	II	−0.84	3.36		112	−1.61	8.04		126
	III	−1.75	21.40						
First fractionation: Liquid fractn.	I	−0.55	13.68	3.5	44	−0.93	10.77	1.4	78
	II	−0.83	3.90		96	−1.52	7.77		120
	III	−1.77	21.16						
Second fractionation: Solid fractn.	I	−0.57	18.26	4.3	50	−0.95	9.84	1.08	66
	II	−0.86	4.28		78	−1.64	8.76		126
	III	−1.71	20.49						

[a] Slope defined by $(E_{1/4}-E_{3/4})$, where $(E_{1/4}-E_{3/4}) = 0.056/n$ at 25° for a reversible process, and $0.056/\alpha n_a$ for an irreversible process.

Consequently, the impurities must aid film formation; addition of water to the sample solution produces the same effect, *i.e.*, a lowering of the entire wave pattern with respect to current.

The maximum in the electrocapillary curve at −0.50 V and the subsequent depression between −0.80 and −1.2 V (Fig. 3) can apparently be associated with the film formation.

Tetraethylammonium solutions

The electrocapillary maximum in purified pyridine is at −0.38 V.

The effect of impurities on the electrocapillary curve is negligible in the absence of oxygen. Curves taken in the presence of oxygen show some deviation from one another with changes in the solvent purity, but these are insufficient to permit any conclusions to be drawn.

More pronounced effects are observed for polarograms of Et_4NClO_4 solutions (Fig. 5; Table II). As the purity of the pyridine is increased, the height of the second reduction wave relative to that of the first wave increases and both half-wave potentials shift to more negative potential with the shift for the second wave being much more pronounced.

Addition of water had effects on the first and second oxygen reduction waves in air-saturated 0.1 *M* Et_4NClO_4 solution in purified pyridine similar to those observed as the purity of the pyridine used was decreased. As the water content increased, the ratio of the first to the second wave in the purified pyridine solution increased from an initial value of 1.08 to 3.55 in the presence of 0.62% water; at the same time, the half-wave potential of the first wave shifted from −0.95 to −0.91 V and that of the second wave from −1.62 to −1.40 V. It seems reasonable to assume from these observations that water has a pronounced effect on the mechanism of the oxygen reduction in tetraethylammonium perchlorate solutions and that zone fractional crystallization of pyridine removes water from the solvent.

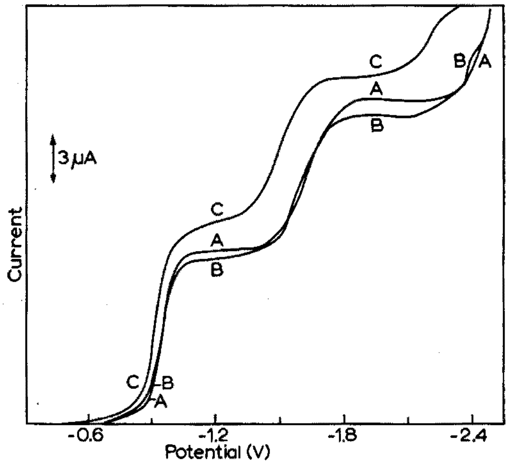

Fig. 5. Polarograms of air-saturated 0.046 M Et_4NClO_4 solutions in various grades of pyridine. A, B and C: as in Fig. 2.

FREE RADICAL STABILITY

As a qualitative test of the effect of the impurity concentration on the stability of a free radical, 1–2 mg amounts of the free radical diphenylpicrylhydrazyl (DPPH) were dissolved in *ca.* 50 ml of purified and of reagent-grade Baker & Adamson pyridine (Lot No. Z069), which were saturated with oxygen and stored in the dark (DPPH undergoes photolytic decomposition). The solution in reagent-grade pyridine changed from violet to yellowish-brown almost immediately indicating a loss of the hydrazyl, which is violet in color. After 7 h, the solution in purified pyridine still retained some violet color but was changing to yellowish-brown; after standing overnight, the degradation was complete. A product of this reaction has been isolated and identified by means of its infrared spectrum as diphenylpicrylhydrazine, which is formed on reaction of DPPH with compounds containing an active hydrogen. This would indicate that the impurities include one or more active hydrogen compounds (the latter does not include water, since the addition of water to a solution of DPPH in pyridine has no apparent effect).

CONCLUSIONS

Voltammetric studies to be made in pyridine should include examination of the effect of impurities in the solvent on the electrode reaction being studied; if these effects are found to be adverse, purification of the pyridine should be undertaken. It would be desirable to require purification for all work in pyridine, *e.g.*, by a satisfactory method such as that described in the present paper. Work is now in progress on the mechanism of oxygen reduction in purified pyridine.

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SUMMARY

Purification of pyridine by zone fractional crystallization reduces the concentration of prewave-producing contaminant below polarographic detection limits, *i.e.*, 0.01 mM. A qualitative test based on the stability of the free radical diphenylpicrylhydrazyl has shown the method to be capable of reducing the concentration of proton-releasing impurities. Water is also removed. Investigation of the effect of the contaminants in normal reagent-grade pyridine on the electrocapillary curves and polarograms of pyridine solutions containing lithium perchlorate and tetraethylammonium perchlorate as background electrolytes in the presence and absence of oxygen, has indicated that the impurities are capable of changing the mechanism for the electrochemical reduction of oxygen in pyridine.

RÉSUMÉ

La purification de la pyridine par cristallisation fractionnée permet de réduire la concentration des contaminants en dessous des limites de détection polarographique (0.01 mM). On a examiné l'influence des contaminants de la pyridine sur les courbes électrocapillaires et sur les polarogrammes à l'aide de solutions pyridine contenant du perchlorate de lithium et du perchlorate de tétraéthylammonium comme électrolytes de base, en présence et en l'absence d'oxygène. On constate que les impuretés peuvent changer le mécanisme de la réduction électrochimique de l'oxygène dans la pyridine.

ZUSAMMENFASSUNG

Die Reinigung von Pyridin durch fraktionierte Zonenkristallisation verringert die Konzentration von Vorstufen erzeugenden Verunreinigungen unterhalb der polarographischen Nachweisgrenze von 0.01 mM. Ein qualitativer Test, der auf der Stabilität des freien Radikals Diphenylpicrylhydrazyl beruht, zeigte, dass diese Methode im Stande ist, die Konzentration von protonenlösenden Verunreinigungen zu verringern. Wasser wird ebenfalls beseitigt. Die Untersuchung des Einflusses der Verunreinigungen in normal reinem Pyridin auf die Elektrokapillaritätskurven und auf die Polarogramme von Pyridinlösungen, die Lithiumperchlorat und Tetraäthylammoniumperchlorat enthalten, in Gegenwart und Abwesenheit von Sauerstoff zeigten, dass die Verunreinigungen im Stande sind, den Mechanismus der elektrochemischen Reduktion von Sauerstoff in Pyridin zu ändern.

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THE APPLICATION OF SUBSTOICHIOMETRIC RADIOISOTOPIC DILUTION PRINCIPLES TO CONTROLLED-POTENTIAL COULOMETRY AND SOLVENT EXTRACTION*

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The application of radioisotope dilution to elemental analysis involves the transfer of mass from one phase to another in order to isolate the desired element in pure form for the purpose of measuring specific activity before and after radioisotope dilution[1]. This process involves heterogeneous equilibrium and can be expressed by the following equations if the reaction goes to completion.

$$yM+zB=y\,MB'+(z-y)\,B \tag{1}$$

$$(y+x)\,M+zB=(y+x)\,MB'+(z-x-y)\,B \tag{2}$$

where y = atoms of the radioisotope, M, in phase 1
z = atoms of excess reagent, B, in phase 1
x = atoms of element to be determined

and the prime indicates the presence of the 1:1 compound or complex MB in phase 2. If the y radioactive atoms of M have specific activity A_1 (*e.g.* counts $\text{min}^{-1}\ \text{g}^{-1}$) and the dilution of these atoms with x inactive atoms of M results in specific activity A_2 where $A_2 < A_1$, then equating the total radioactivity before and after dilution of the separated species MB′ gives:

$$YA_1=(X+Y)\,A_2 \tag{3}$$

where: $A_1=a_1/m_1$ and $A_2=a_2/m_2$, and where m_1 and m_2 are the amounts of element M, and a_1, a_2 are the radioactivities isolated as MB′ before and after dilution, respectively, X is the unknown amount of element M and Y is the total amount of element M in the radioisotope. An amount of MB′ which can be an arbitrary fraction of the total amount of M in phase 2 can then be isolated in pure form. By measuring m_1, m_2, a_1, and a_2 and by knowing Y, the value of X can be calculated.

For trace elemental analysis, the measurement of m_1 and m_2 presents difficulties since gravimetric procedures are most often used. RŮŽICKA AND STARY[2] suggested that if the process of purification, separation and the measurement of specific activity could be combined, a suitable trace analytical method would be possible. They used a substoichiometric amount of reagent in accordance with the equations:

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* This work was carried out at the National Bureau of Standards and taken in part from the Ph.D. thesis of P. A. PELLA, University of Maryland, 1967.

$$yM + zB = z\,MB' + (z-y)\,M \tag{4}$$

$$(y+x)\,M + z\,B = z\,MB' + (y+x-z)\,M \tag{5}$$

where $z < (x+y)$.

This results in making $m_1 = m_2$ and eqn. (3) becomes:

$$Ya_1 = (X+Y)a_2 \tag{6}$$

The conditions must be carefully controlled so that only the element of interest reacts with the reagent and that 99.9% of the reagent is reacted. If this is the case then the introduction of the additional amount x of M in eqn. (5) does not appreciably increase the amount of MB′ isolated.

To test whether or not a given heterogeneous reaction is operating in the substoichiometric concentration region, eqn. (6) is used in the form:

$$a_1/a_2 = X/Y + 1 \tag{7}$$

A plot of a_1/a_2 *vs.* X for constant Y should give a straight line.

If the substoichiometric radioisotope dilution (SRD) principle does not apply, and the relationship between m_2 and X is known (*e.g.* from the law of mass action in the particular equation given) then a similar relationship can be used to give a straight line[3,4].

$$\frac{a_1}{a_2}\,\frac{f(X+Y)}{m_1} = \frac{X}{Y} + 1 \tag{8}$$

This can be considered to be a concentration-dependent (CDM) method of SRD. This procedure is a more generalized technique in that it can be used for samples in which interferences exist from the presence of other elements in the sample which also interact with the reagent. This is true as long as an empirical or theoretical relationship between m_2 and X can be found[5]. Such a method could be considered analogous to the classic method of standard additions. The method of standard additions can also be used, of course, when the SRD principle applies. This simply involves adding known amounts of stable element to result in increasing the value of X.

It should now be clear that any process involving heterogeneous equilibrium such as ion exchange[3], extraction[5], electrochemistry, etc., can be used with these principles. A description of the use of these techniques in solvent extraction and electrochemistry is given below.

The controlled-potential coulometric procedure uses 2 identical electrolytic cells which are connected in series. Under prescribed conditions the same amount of the element is deposited in each cell. This permits the application of the SRD technique.

The procedure involves the addition of a known amount of the element to be analyzed to the control cell which is held at a constant potential and an unknown amount to the sample cell. An equal known amount of a radioisotope of that element is added to each cell. Since the same amount is deposited in each cell, the unknown amount may be determined by measuring the radioactivity left in each of the cells after a finite electrolysis time. The relationship derived from eqn. (3) can be written in the form

$$\Delta M = M(a_2 - a_1)/(a_t - a_2) \tag{9}$$

where ΔM is the differential, M is the known amount added to the control cell, a_1 and a_2 refer to counts per minute of a radioisotope of element M left in the control and sample cells respectively, and a_t is the total amount of radioactivity in counts per minute added initially to each cell.

In order to obtain independent verification of the series controlled-potential method and to establish a means of comparison with the radioisotope technique a current integration procedure was also used[5,6].

A micro technique using solvent extraction for ideal solutions of cadmium in the concentration region where SRD applies was developed. In addition the sensitivity of the technique was improved by operating in the concentration region where the CDM or SRD applies. To show its applicability to real samples, a Standard Reference Material No. 108 (zinc spelter) and a high-purity zinc were analyzed. After the cadmium had been separated from the zinc matrix, the method of standard additions using the SRD technique was used.

EXPERIMENTAL

Differential controlled-potential coulometry utilizing radioisotopes

Apparatus. A diagram of the electrolysis cells employed is shown in Fig. 1. Both the control and sample cells are identical.

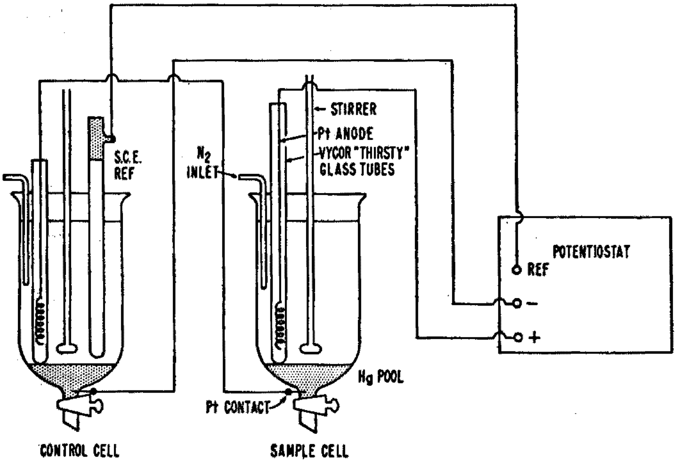

Fig. 1. Apparatus for differential controlled-potential coulometer utilizing radioisotopes.

The anode consists of a platinum wire bent in the shape of a helix and is isolated from the solution by a "Thirsty"* vycor glass tube about 0.35 in × 5.5 in. The glass tube is of low electrical resistance. The reference electrodes used are identical saturated calomel electrodes of the commercial type with a porous pin liquid

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* Corning Glass Co. In order to specify adequately the procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by NBS, nor does it imply the material or equipment identified is necessarily the best available for the purpose.

junction. The cathodes are mercury pools about 7 cm^2 in area. The solution and pools are stirred by means of a glass stirring rod fitted to a synchronous motor assembly and rotated at 1800 rev./min. The cell cap is fabricated from lucite of 1-in thickness. In addition to the holes drilled for the anode, reference electrode, stirrer, and nitrogen inlets, a hole drilled diagonally permitted the introduction of sample solutions into the cell without removal of the cap. This provision was convenient in that a positive nitrogen pressure could be maintained inside the cell while solutions were being introduced.

For studies at the microgram level, the entire cell assembly was enclosed in a dry box made of durable plastic and was filled with nitrogen before the start of the experiment. Withdrawal of the solutions from the cells was accomplished by inlets in each cell which were attached to a common vacuum pump.

The potentiostat used in these experiments was built according to the design of CONNALLY AND SCOTT[7]. The current integration equipment consisted of a voltage-to-frequency converter, scaler, timer, and constant-current calibration source. Counting equipment consisted of an automatic sample changer and scintillation counter with a well-type NaI(Tl) crystal. Potentials were measured with a millivolt potentiometer.

Reagents. Stock solutions of cadmium were prepared by dissolving high-purity cadmium metal (99.99%) in a minimum amount of concentrated hydrochloric acid and filling to volume with distilled water in volumetric flasks. The distilled water was purified by passing it through a mixed bed ion exchanger. The supporting electrolyte was prepared by dissolving analytical-reagent grade potassium nitrate in distilled water. Further purification of this solution when required was accomplished by electrolysis at controlled potential at −1.0 V *vs.* S.C.E. A cadmium-109 stock solution was prepared by dilution of a 5-mC cadmium-109 solution of high specific activity. Working solutions were prepared by dilution of the appropriate volumes of the cadmium metal and cadmium-109 stock solutions in volumetric flasks.

Procedure A (Radioisotope dilution). To each of the cells was added 3.00 ml of 0.1 N potassium nitrate followed by 1.00 ml of cadmium solution containing ^{109}Cd. These solutions were previously deaerated by passing prepurified nitrogen first through a gas tower containing 0.1 N potassium nitrate and then through these solutions. Each cell was preelectrolyzed at −0.40 V *vs.* S.C.E. to remove traces of oxygen. Electrolysis was continued until the residual current in each cell was identical. With the cells in series, the control cell potential was held at −0.75 V *vs.* S.C.E. and the time of electrolysis was either 5 or 10 min. Without interruption of the electrolysis, samples of solution were *simultaneously* withdrawn from each cell. Then 1.00 ml of each solution was transferred to a counting tube, placed in the radiation detector and counted until 100,000 counts were accumulated.

Procedure B (Current-integration). The same preelectrolysis procedure was carried out as described above. With the cells in series and control cell potential at −0.75 V *vs.* S.C.E., electrolysis was carried out to completion until the residual current was reached. The potential control was then immediately transferred to the sample cell where integration of the current was recorded until the same value of residual current as obtained in the control cell was reached. The time of electrolysis in each case was about 35 min. The residual current was then integrated for the same length of time and its contribution subtracted from the entire integral. A technique similar to that described above has been used by RECHNITZ AND SRINIVASAN[6].

Microtechnique using solvent extraction of cadmium with dithizone

Reagents. See references 5 and 8 and the reagents listed above. Solution A was prepared by mixing 10.00 ml of 20% sodium potassium tartrate, 5.00 ml of 10% hydroxylamine hydrochloride, 15.00 ml of an ammonia–ammonium chloride buffer (pH 10) and 0.025 ml of carrier-free cadmium-109 and was diluted to volume in a 50.00-ml flask.

Procedure C (SRD and CDM). A cadmium solution (100 μl) containing $1 \cdot 10^{-6}$ g/ml was pipetted into a 2-dram vial, and 100 μl of a cadmium solution containing 0.20 μg Cd and 300 μl of solution A was added. The vials were stoppered and shaken gently for 2 min. The solutions were extracted with 500 μl of dithizone in chloroform (0.002 mg/ml). After the chloroform addition to the sample, the vials were restoppered and shaken manually for 2–3 min. The samples were each transferred to 2-ml glass centrifuge tubes in order that the two phases could become clearly distinguishable. Immediately 50-μl aliquots of both phases were pipetted into counting tubes.

For the concentration-dependent method (CDM) of SRD, the procedure was the same as above except that lower concentrations of cadmium (0.26 to 0.01 μg) were used.

Analysis of high-purity zinc and standard reference material 108 (zinc spelter). The cadmium was separated from the zinc by the following procedure. A sample of high-purity zinc which weighed 24.854 g (6.0021 g for SRM 108) was dissolved in 6 N hydrochloric acid and the solution was made up to volume in a 50.0-ml volumetric flask. The contents of this flask were transferred to an electrolytic cell. The cathode consisted of a mercury pool about 13 cm^2 in area. The potential of the cathode was controlled at -0.900 V *vs.* S.C.E. for 12–14 h. Carrier-free cadmium-109 was added to the sample before electrolysis, enabling one to determine the yield throughout the separation. The cadmium was deposited in the mercury as an amalgam whereas the zinc was left in solution. The aqueous solution containing the zinc was drawn off, care being taken not to break the electrical contact. After the zinc solution had been removed, the amalgam was washed continuously with a liter of 0.1 N perchloric acid. Shaking of the amalgam in contact with the acid solution was accomplished by placing the amalgam in an ultrasonic cleaner for 2 h. The perchloric acid solution contained mercury and cadmium. The cadmium was extracted from the perchloric acid solution using five 100-ml aliquots of a solution containing 0.20 mg of dithizone per ml. Most of the cadmium was extracted in the second and third portions. The combined chloroform extract was evaporated to a small volume and extracted with 30 ml of 1 N nitric acid. When this solution was evaporated to 5 ml and made basic with ammonia, a fine white precipitate of $HgNH_2OH$ appeared. The solution was filtered through a millipore filter, evaporated and diluted to 2.00 ml in a volumetric flask.

Ten 100-μl aliquots of this solution were then processed. To 5 of these no stable cadmium was added. To the other 5 known amounts of stable cadmium were added and the SRD technique described in Procedure C was used. This is the method of standard additions described in more detail elsewhere[5,8]. The blank was subjected to the same procedure as the sample.

RESULTS AND DISCUSSION

Table I includes the data obtained by the controlled-potential coulometric method for ideal solutions with both the SRD and the current integration procedures. Comparison of the techniques at this concentration level leads to the conclusion that the precision (expressed as standard deviation of a single measurement) of the integration procedure is greater; however, the accuracy attained as shown in the Table is comparable. It can also be said from this study that for this concentration level the accuracy of the amount determined in the sample cell becomes greater as the differential becomes smaller. The same conclusion was expressed in a similar study[6].

TABLE I

RADIOISOTOPE METHOD FOR DIFFERENTIAL CONTROLLED-POTENTIAL COULOMETRY

Control cell (μg)	*Sample cell (μg)*	*Found mean (μg)*	*% Rel. error*	σ_s[a] *(μg)*	*No. of detns.*
200.05	400.19	396.33	−0.96	3.44	5
248.93	400.19	401.80	+0.40	3.15	5
323.16	400.19	399.22	−0.24	2.56	5
381.18	400.19	400.81	+0.16	2.39	6
19.02	38.51	38.35	−0.42	0.71	6
22.92	38.51	38.29	−0.57	0.60	6
26.71	38.51	38.58	+0.18	0.79	7
30.53	38.51	38.27	−0.62	0.44	5
2.15	4.25	4.15	−2.35	0.11	5
2.15	2.97	3.01	+1.35	0.20	5
2.15	2.15	2.08[b]	−3.26	0.10	5
Integration method					
200.05	400.19	397.06	−0.78	1.25	6
248.93	400.19	397.45	−0.68	1.49	5
323.16	400.19	401.11	+0.23	0.76	4
381.18	400.19	400.69	+0.12	0.70	6

[a] σ_s = Standard deviation.

[b] Stirring rate in control cell reduced to 900 rev./min.

The sensitivity of the method can be increased by use of an inert nitrogen dry box which provides a minimum of oxygen interference and preelectrolysis of the supporting electrolyte which greatly reduces the electroactive contaminants which can affect the analysis. The sensitivity of the method can also be increased by using radioisotopes of high specific activity and by using a "micro cell" for the analysis in order to reduce the residual current.

The data obtained for ideal solutions of cadmium by the microsolvent extraction procedure are shown in Table II. For comparison some previous results by the regular SRD technique[8] are shown in Table III. The micro method has a higher sensitivity than the regular solvent-extraction procedure with a decrease in the accuracy, but no appreciable decrease in precision.

The precision and accuracy of these microtechniques may be affected by a number of factors. The most serious errors affecting the precision are caused by the evaporation of the organic phase and oxidation of the dithizone. It is evident at

TABLE II

DETERMINATION OF CADMIUM BY USING MICROSOLVENT EXTRACTION PROCEDURE[a]

μg added *X*	*Found mean (μg)*	*% Rel. error*	σ_s *(μg)*	*No. of detns.*
0.500	0.470	+6.00	0.010	4
0.400	0.407	−1.75	0.006	4
0.300	0.272	−9.33	0.004	4
0.200	0.175	−12.50	0.005	4
0.100	0.103	+3.00	0.004	4

[a] $Y = 0.20$ μg, total volume aqueous phase 500 μl; 500 μl of 0.002 mg/ml dithizone used for extraction.

TABLE III

DETERMINATION OF CADMIUM BY SOLVENT EXTRACTION[a]

Added (μg)	*Found mean (μg)*	*% Rel. error*	σ_s *(μg)*	*No. of detns.*	*Concn. of dithizone (mg/ml)*
100.0	97.0	−3.00	3.00	5	0.2
10.00	10.2	+2.00	0.20	5	0.02
1.00	1.03	+3.00	0.03	5	0.002

[a] Vol. organic phase 5 ml; vol. aqueous phase 5.00 ml.

the submicrogram level that contamination due to reagents, apparatus, and airborne contamination may affect the accuracy as well as the precision.

NBS Standard Reference Material 108, zinc spelter, and high-purity zinc were analyzed for cadmium. The matrix has a profound effect on the accuracy of this method and it was necessary to use the method of separation described above. The recommended value for sample No. 108 is 10.97 μg/ml corresponding to 0.092% and the amount found was 10.64 μg/ml (average of 5 determinations with a $\sigma_s = \pm 0.16$ μg standard deviation for a single determination). The relative error was 3.01%. If the standard addition method is not used the precision is about the same, but the relative error is about 6%.

The high-purity zinc sample was also analyzed by the method of standard addition. The amount of cadmium found for 5 runs was 0.16 μg with σ_s of 0.09 μg for a single determination of cadmium per gram of sample. In order to analyze this sample it was necessary to use the method of separation and preconcentration described above. Losses were corrected for by the use of tracers and a blank correction was also made. The large error in the amount obtained is due to the high blank. Although the blank was always less than the value of the sample it was obvious that this method was operating at its limit of detection. It was found that the sample contained less than 0.3 μg at the 95% confidence level.

In an effort to improve the limit of sensitivity, an empirical method using the CDM was developed. A standard curve for ideal solutions is shown in Fig. 2. The straight line is the result of a least squares analysis of the data. It is evident that the sensitivity has been improved by this graphical method. The advantages of this graphical procedure are that the amount in the tracer need not be known and it is evident that the total elemental concentration of the tracer can be determined by means of this approach. Also, when the amount in the tracer is small or well known, one can apply a method of standard additions.

The blank for the total analysis and the specific activity of the radioisotopes are the two most important factors that limit the sensitivity. Microtechniques and methods of preconcentration accentuate the problem, but with care very high sensitivity can be reached. The precision and accuracy obtained compare favorably with other trace analytical techniques for cadmium.

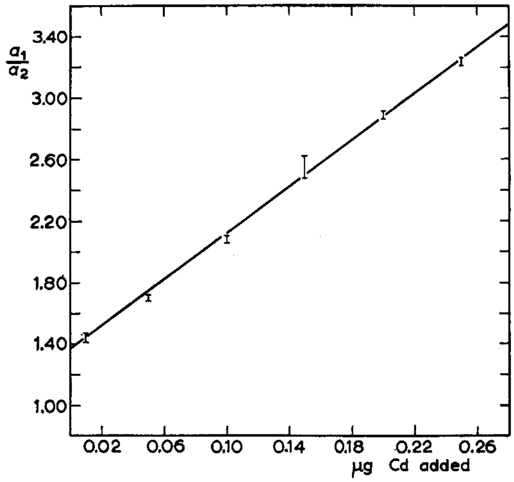

Fig. 2. Concentration dependent method (CDM) microsolvent extraction procedure for cadmium.

SUMMARY

Radioisotope dilution principles are applied to controlled-potential electrolysis and solvent extraction with dithizone for the determination of trace amounts of cadmium. A method was developed to verify whether or not the substoichiometric principle was obeyed. If the substoichiometric principle was not obeyed, analysis was still possible by means of calibration curves. In order to obtain independent verification of the series controlled-potential method and to establish a means of comparison with the radioisotope dilution technique a current integration procedure was also employed. A microtechnique was used to extend the sensitivity of the solvent extraction system for cadmium. Standard zinc spelter and high-purity zinc were analyzed for cadmium after separation by a method of standard addition.

RÉSUMÉ

On a appliqué les principes de dilution radioisotopique à l'électrolyse à potentiel contrôlé et à l'extraction dans un solvant, au moyen de dithizone pour le dosage de traces de cadmium. Afin de réaliser une vérification indépendante de la méthode à potentiel contrôlé et d'établir un moyen de comparaison avec la technique par dilution isotopique, on peut utiliser également un procédé d'intégration de courant. Une microméthode permet d'améliorer la sensibilité du système d'extraction pour le cadmium.

ZUSAMMENFASSUNG

Die Radioisotopenverdünnungs-Technik wurde auf die Elektrolyse mit kontrollierten Potentialen und die Flüssigextraktion mit Dithizon zur Bestimmung von Spuren Cadmium angewandt. Dazu wurde eine Methode zur Prüfung, ob die substöchiometrische Technik befolgt wird, entwickelt. Eine Mikrotechnik wurde zur Steigerung der Empfindlichkeit der Flüssigextraktion des Cadmiums verwendet.

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LINE SOURCES IN ABSORPTION SPECTROSCOPY

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It has been recognized that a continuous source, as used with conventional spectrophotometers, presents several disadvantages and is not an ideal source for absorption spectrophotometric measurements. The energy emitted from such a spectral source is not monochromatic radiation, as required by Beer's law. Furthermore, no reference calibration point is available to check the accuracy of the wavelength dial. Thus, the mean wavelength position and the resultant spectral band width are not generally reproducible from one instrument to another. The difficulties associated with non-monochromatic radiation are well known; non-linear working curves and reduced sensitivity are obtained. These disadvantages become more important when measurements are made on a sharp absorption band where slight variations in the wavelength or within the spectral band will create marked changes in the observed absorbances. Also, since the monochromator transmits a finite band of radiation, as determined by the slit width, the detector will indicate the average intensity over the band, which is not necessarily the true absorbance at the central specified wavelength of interest. If a monochromatic source were available, such experimental difficulties would be obviated.

A mercury arc has been used by TUNNICLIFF[1] to analyze mixtures of aniline, N-methylaniline, and N,N-dimethylaniline. A similar source was used by HADDEN AND PERRY[2] to determine styrene in ethylbenzene, and by GILBERT *et al.*[3] to determine lithium carbide in metallic lithium as the acetylene–silver perchlorate complex. The recent development of atomic absorption spectroscopy has made available a large variety of hollow-cathode tubes, sharp line monochromatic sources which are necessary for the narrow absorption bands of the atomic states. Although the absorption band of the molecular state does not require such a narrow band width of incident radiation, there would still be important advantages to the availability of these line sources for certain applications. This investigation was designed to study the utility and advantages of hollow-cathode tubes and discharge lamps as line sources for spectrophotometric investigations of sharp absorption spectra.

EXPERIMENTAL

Reagents

Practical grade cyclohexane (Matheson, Coleman, and Bell) was purified for use as a spectral solvent by chromatography with a 80–200 mesh alumina (Fisher) and 20–200 mesh silica gel (Will) column. C. P. grade benzene (Allied) was dried, distilled, and stored over sodium. A stock solution was prepared by dissolving 0.4853 g of redistilled benzene in 100 ml of purified cyclohexane. Working solutions were prepared by weighing out appropriate amounts of the stock solution, ranging from 0.7489 g to 11.5111 g, and diluting to 100 ml with cyclohexane to give a range of absorbances from about 0.10 to 1.50.

p-Cresol (Matheson, Coleman, and Bell) was distilled, twice recrystallized from purified cyclohexane, and then sublimed to effect purification. Stock and working solutions were prepared in an analogous manner to benzene. Anthracene (Aldrich) was twice recrystallized and then sublimed. Stock and working solutions were again prepared as previously described.

Reagent grade 70% perchloric acid (Baker and Adamson) was diluted with distilled water to prepare 1 *M* perchloric acid solution.

Solutions were prepared from neodymium oxide and holmium oxide (Matheson, Coleman, and Bell), 99.9%, as follows: 5.8814 g of Nd_2O_3 were dissolved in 100 ml of 1 *M* perchloric acid to prepare a stock solution. Small amounts of the stock were pipetted and weighed into 10-ml volumetric flasks, diluted to volume, weighed again, and the exact concentrations calculated. Five working solutions were prepared to give absorbances from about 0.20 to 0.90. 2.0690 g of Ho_2O_3 were dissolved in 25 ml of perchloric and similar working solutions prepared.

Apparatus

A Beckman DU was modified by replacing the conventional blue and red phototubes with 1 P28 and 1 P22 photomultiplier tubes and measuring the output currents by means of a Heath recording electrometer[4]. The photomultipliers were powered by a variable output battery power supply with coarse and fine controls. The hydrogen and tungsten continuous sources were powered by a Beckman hydrogen lamp power supply and a 6-V constant voltage transformer, respectively. The monochromatic sources were mounted on a Cenco 66 centimeter optical bench by means of a standard rider and clamp combination. A 1-inch quartz lens (5-inch focal length), also mounted on an optical bench rider, focused the light beam onto the entrance slit of the monochromator.

The Westinghouse hollow-cathode tubes were powered by a Kepco Model ABC 425M, 0.05% regulated power supply, operated in the constant current configuration. The cadmium discharge lamp, operated at 1.5 A, was powered by a Spectroline Discharge Lamp Power Supply, Series 1500.

Four Beckman quartz cells were selected to match to within 1% transmittancy. Correction factors were applied to compensate for this difference.

The atomic absorption studies were performed on a Hitachi–Perkin-Elmer Model 139 spectrophotometer used with a Perkin-Elmer slot atomizer-burner and associated optical train to form a DC atomic absorption system.

Results and discussion

A comparative study of the monochromatic and continuous sources was first carried out. When the relative intensity of each source was plotted against spectrometer slitwidth, a quadratic response was obtained from the tungsten and hydrogen lamps while the expected linear plot was obtained from the hollow-cathode tubes and discharge lamps. The linear response of the monochromatic sources was observed as long as the slitwidth was sufficiently narrow to exclude any adjacent spectral lines.

The hollow-cathode tube current was varied to determine its effect on the monochromatic radiation intensity. Over the current ranges studied, 5–15 mA for the magnesium tube and 5–40 mA for the copper tube, the output intensity increased as the square of the current. A straight line resulted from the plot of square root of relative intensity *versus* tube current.

The advantages of monochromatic sources over conventional continuous sources would be most pronounced in the case of a sharp absorption band system. Although most ultraviolet-visible molecular absorption spectra show broad, diffuse bands, certain aromatic compounds, as well as many of the rare earths, exhibit relatively sharp absorption bands which serve to illustrate some of the advantages of monochromatic radiation. The choice of compounds for study is of necessity limited to those which have absorption bands overlapping with the line available from the monochromatic source. Of the organic systems, benzene, *p*-cresol, and anthracene met these criteria. Neodymium and holmium were selected from the rare earths. An absorption spectrum of each compound in solution was obtained with a Beckman DK-2. The narrow band of analytical interest was then more carefully defined by manual measurements with the previously described single-beam spectrometer.

For the study of benzene solutions, the 2492.15 Å copper line (0–40114 K) from the copper hollow-cathode tube was used since the maximum of one of the benzene absorption bands occurs at approximately this wavelength. The 3403.65 Å cadmium line (30114–59486 K) from the cadmium discharge lamp was selected for the anthracene solutions, and the 2852.13 Å magnesium line (0–35051 K) from the magnesium hollow-cathode tube was chosen for the *p*-cresol solutions because of their favorable locations with respect to the absorption bands of these compounds in solution. For neodymium, the 3466.20 Å (30656–59498 K) and the adjacent unresolved 3467.66 Å (30656–59486 K) cadmium lines were satisfactory while for holmium, another unresolved pair of cadmium lines, 3610.51 Å (31827–59516 K) and 3612.88 Å (31827–59498 K), was selected. Comparison data of line *versus* continuous sources were obtained by setting the wavelength to the monochromatic line as determined by maximum readout intensity, then substituting the continuous source without moving the wavelength dial.

In the case of the hollow-cathode lines, the effect of tube current on absorption was investigated. With copper and magnesium test solutions, atomic absorption studies showed a decrease in absorbance as the tube current was increased up to the maximum safe limits, indicating a probable increase in line width. When the effect of the same variation in tube current was studied with respect to the solution absorbance, no change in absorbance was noted. This follows since, although the change in emission line profile is significant compared to the atomic absorption profiles, it is insignificant when considered against the solution absorption bands. Therefore, hollow-cathode tubes when used as monochromatic sources for solution absorption, can be operated at higher currents to increase tube intensity without a sacrifice of sensitivity. Only tube lifetime would be a consideration.

A major advantage to the use of monochromatic sources would be the fact that the monochromator slitwidth should have little effect on absorbance sensitivity if only the analysis line is passed at the effective spectral band pass. Thus, in the case of the Beckman DU used in this investigation, a maximum slitwidth of 2.00 mm might well be an acceptable value for a line source whereas a comparable slit setting for a continuous source would be experimentally infeasible. Plots of absorbance *vs.* slitwidth were constructed for all the compounds previously listed; typical results are shown in Figs. 1 and 2. Figure 1 shows, for a holmium solution, the linear, constant absorbance resulting from the use of the cadmium discharge lamp as spectral source and the rapid change in absorbance produced when a continuous source is used. Data obtained with the hollow-cathode tubes as sources is similar. Figure 2 shows the results, for anthracene, of picking up an adjacent spectral line as the band pass is widened.

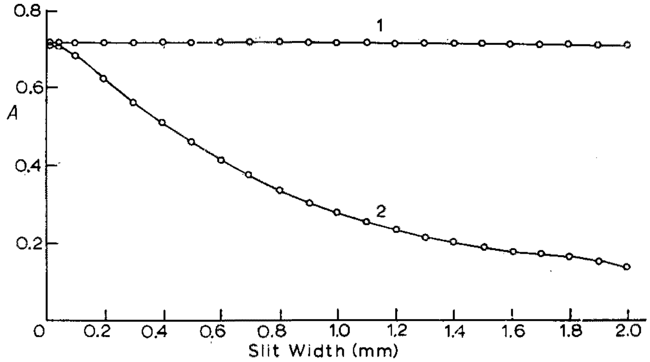

Fig. 1. Absorbance *vs.* slitwidth for holmium at 3611 Å using as a source (1) a cadmium discharge lamp and (2) a hydrogen lamp.

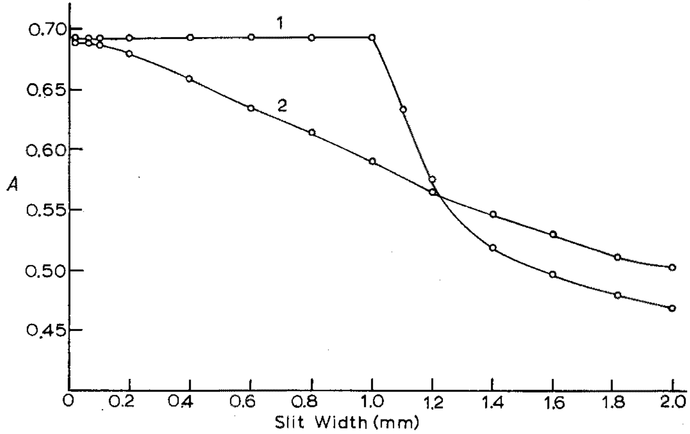

Fig. 2. Absorbance *vs.* slitwidth for anthracene in cyclohexane at 3404 Å using as a source (1) a cadmium discharge lamp and (2) a hydrogen lamp.

Working curves were constructed from the standard solutions for each test compound to determine the relative sensitivity and adherence to Beer's law as a function of monochromator slitwidth. Typical plots are shown in Figs. 3 and 4. A single slope represents the data obtained from the monochromatic source, since there was essentially no change in absorbance as the slitwidth was increased to the maximum of 2.00 mm. The effect of a continuous source is reflected in the lower sensitivities and the deviations from linearity as the spectral band width widens.

There is no reason to suggest a wide use of monochromatic sources for absorption spectrophotometry since their application would seem to be advantageous only to rather specialized applications. For systems exhibiting sharp absorption bands, there is some increase in sensitivity using a monochromatic source, particularly if instrumental limitations prohibit a narrow slitwidth with the conventional continuous source. However, other advantages should be considered. The uncertainty of reproducibly setting the analysis wavelength, a critical factor in the case of sharp absorption bands, is eliminated by merely adjusting the wavelength dial to a maximum signal response on the analysis line as emitted by the line source. The exact wavelength will be that given for the line, eliminating any discrepancies in wavelength scale calibration. The line source would act as a means of calibration for the monochromator, since several lines are normally available throughout the wavelength scale. A further advantage is the relative unimportance of the slitwidth. This allows the operation of a spectrophotometer under excellent signal-to-noise conditions. A wide slitwidth results in a high line source intensity which allows the use of low photomultiplier voltage, low amplifier gain, and modest readout sensitivity ranges.

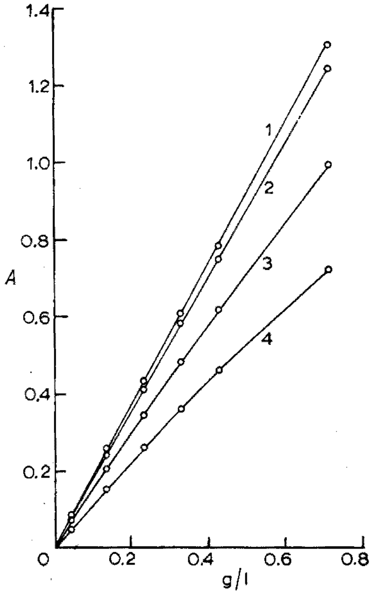

Fig. 3. Working curve for benzene in cyclohexane at 2492 Å. (1) Copper hollow-cathode tube source; (2) H_2 lamp, 0.05-mm slit; (3) H_2 lamp, 1.00-mm slit; (4) H_2 lamp, 2.00-mm slit.

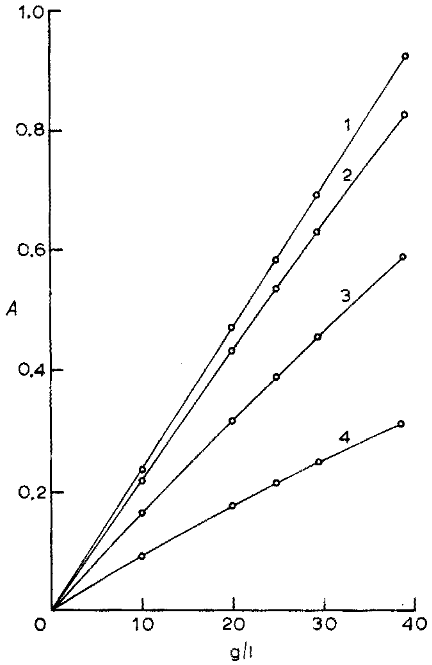

Fig. 4. Working curve for neodymium solutions at 3467 Å. (1) Cadmium discharge lamp source; (2) H_2 lamp, 0.05-mm slit; (3) H_2 lamp, 0.20-mm slit; (4) H_2 lamp, 1.00-mm slit.

In selecting an analysis line, there is no necessity for the line to be at the exact absorption maximum. If a small sensitivity concession is possible, a line which falls somewhat to either side of the absorption peak is quite satisfactory since there is no experimental difficulty in reproducibly setting this wavelength. The use of monochromatic sources should also allow more reasonable comparison of absorption data taken from similar instruments. Errors resulting from differences in calibration of the two wavelength scales would be eliminated.

Differential spectrophotometry represents an experimental area where a line source may be of importance. The scale expansions associated with this technique often require the use of a wider slit to maintain a sufficient source intensity. With a continuous source, this would then act to reduce sensitivity as the band pass widened. An isolated monochromatic line could be used at a varying slitwidth with little or no sensitivity decrease.

SUMMARY

Hollow-cathode tubes and discharge lamps are studied as spectral sources for absorption spectrophotometry. Comparisons are made of monochromatic *versus* conventional continuous sources with respect to several experimental parameters, particularly the effect of slitwidth. Working curves are shown to indicate the possible advantages of using line sources for narrow band absorption systems.

RÉSUMÉ

On a examiné les tubes à cathode creuse et les lampes de décharge comme sources spectrales pour spectrophotométrie par absorption. Des comparaisons ont été faites avec les sources conventionnelles pour plusieurs paramètres expérimentaux, en particulier l'influence de la largeur de fente. Des courbes montrent les avantages possibles de l'utilisation de sources linéaires pour les systèmes d'absorption à bande étroite.

ZUSAMMENFASSUNG

Hohlkathoden-Röhren und Entladungslampen werden als spektrale Quellen für die Flammenabsorptionsspektralanalyse untersucht. Für verschiedene experimentelle Parameter, besonders den Einfluss der Spaltbreite, werden die monochromatischen Quellen mit den konventionellen, kontinuierlichen verglichen. Es werden die möglichen Vorteile der Linienquellen für schmale Banden aufgezeigt.

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TITRATION CURVES OF COMPLEXIMETRIC TITRATIONS OF MIXTURES OF METAL IONS WITH ONE LIGAND

PART I. MATHEMATICAL EXPRESSIONS

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Several papers have appeared which deal with calculations of titration curves in compleximetric titrations[1–4]. However, no exact mathematical expressions seem to be available for titrations of mixtures of two or more metal ions with one ligand. Such expressions would be of interest, not only to judge the possibilities for end-point detection at all, but also for the selection of the proper indication method. Expressions are derived in this paper in which only two simplifications are introduced. Changes in volume are neglected and concentrations are used instead of activities.

Terminology and symbols

The symbols used are in accordance with present practice in this field of investigation[5], with the exception that concentrations and stability constants are not primed, since only conditional constants and concentrations are used.

[M], [N], [P]	Concentration of the metal ions M, N and P in any form, except the chelates MY, NY and PY in any form.
[Y]	Concentration of the ligand Y in any form, except the chelates MY, NY and PY in any form.
[MY], [NY], [PY]	Concentration of the chelates MY, NY and PY in any form.
c_M, c_N, c_P	Concentration of M, N and P in any form.
c	Total concentration of all metals ($c = c_M + c_N + c_P$).
c_Y	Concentration of Y in any form.
K_{MY}, K_{NY}, K_{PY}	Conditional stability constants of MY, NY and PY.
$f = c_Y/c$	Titration parameter, fraction titrated = $= \dfrac{\text{amount of ligand added in moles}}{\text{total amount of metals in moles}}$
f_1, f_2, f_3	Parts of the mathematical expressions for the titration curves.

Mathematical expressions

It is assumed that only 1:1 complexes are formed and that changes in volume during the titration can be neglected*. With these two assumptions the mathematical expression for the titration curve of a mixture of two metals M and N with a ligand Y can be derived from the following equations:

$$K_{MY} = [MY]/[M][Y] \tag{1}$$

$$K_{NY} = [NY]/[N][Y] \tag{2}$$

$$[M]+[MY] = c_M \tag{3}$$

$$[N]+[NY] = c_N \tag{4}$$

$$[Y]+[MY]+[NY] = c_Y \tag{5}$$

$$f = c_Y/(c_M+c_N) = c_Y/c \tag{6}$$

By means of these equations f, the titration parameter, can be expressed in terms of one of the 5 concentrations [M], [N], [MY], [NY] or [Y] and the known constants K_{MY}, K_{NY}, c_M, c_N and c. Each of these 5 expressions can be considered a titration curve. The expressions for f as a function of [M] can be derived as follows: Combination of eqns. (1) and (3) gives

$$[Y] = \frac{c_M-[M]}{[M]K_{MY}} \tag{7}$$

and eqns. (2) and (4) give

$$[Y] = \frac{c_N-[N]}{[N]K_{NY}} \tag{8}$$

Combination of (7) and (8) gives

$$[N] = \frac{c_N}{(c_M/[M]-1)\,K_{NY}/K_{MY}+1} \tag{9}$$

while eqns. (5) and (6) give

$$f = \frac{c_Y}{c} = \frac{[Y]}{c} + \frac{[MY]}{c} + \frac{[NY]}{c} \tag{10}$$

Substitution of eqns. (3), (5) and (7) in eqn. (10) and rearrangement gives

$$f = 1 - \frac{[M]}{c} - \frac{[N]}{c} + \frac{c_M}{c}\,\frac{1}{[M]K_{MY}} - \frac{1}{cK_{MY}} \tag{11}$$

Substitution of eqn. (9) in eqn. (11) gives an expression for f as a function of [M]

$$f = 1 - \frac{[M]}{c} + \frac{c_M}{c}\,\frac{1}{[M]K_{MY}} - \frac{1}{cK_{MY}} - \frac{c_N}{c}\,\frac{1}{(c_M/[M]-1)K_{NY}/K_{MY}+1} \tag{12}$$

The analogous formula for [N] is

$$f = 1 - \frac{[N]}{c} + \frac{c_N}{c}\,\frac{1}{[N]K_{NY}} - \frac{1}{cK_{NY}} - \frac{c_M}{c}\,\frac{1}{(c_N/[N]-1)K_{MY}/K_{NY}+1} \tag{13}$$

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* With the syringe burettes available at present, it is generally possible for the volume not to change appreciably during a titration. Even when the volume changes cannot be neglected, the expressions derived maintain their value, provided that either a value of c is used which takes into account the dilution at the equivalence point in the case of an indication method for pM or pY, or a correction for volume change is applied in the case of an indication method for [M] or any other concentration.

An expression for f as a function of [Y] can be obtained from eqn. (10), combined with eqns. (7) and (8).

$$f = 1 + \frac{[Y]}{c} - \frac{c_M}{c}\,\frac{1}{[Y]K_{MY}+1} - \frac{c_N}{c}\,\frac{1}{[Y]K_{NY}+1} \tag{14}$$

Substitution of eqn. (3) in eqn. (12) gives f as a function of [MY]

$$f = \frac{[MY]}{c} + \frac{1}{(c_M/[MY]-1)}\,\frac{1}{cK_{MY}} + \frac{c_N}{c}\,\frac{1}{(c_M/[MY]-1)K_{MY}/K_{NY}+1} \tag{15}$$

The analogous expression for [NY] is

$$f = \frac{[NY]}{c} + \frac{1}{(c_N/[NY]-1)}\,\frac{1}{cK_{NY}} + \frac{c_M}{c}\,\frac{1}{(c_N/[NY]-1)K_{NY}/K_{MY}+1} \tag{16}$$

For the titration of three metals M, N and P with one ligand, again on the assumption of 1:1 complexes and no changes in volume, the following titration curves can be derived in exactly the same way:

$$\begin{aligned} f = 1 - \frac{[M]}{c} + \frac{c_M}{c}\,\frac{1}{[M]K_{MY}} - \frac{1}{cK_{MY}} - \frac{c_N}{c}\,\frac{1}{(c_M/[M]-1)K_{NY}/K_{MY}+1} \\ - \frac{c_P}{c}\,\frac{1}{(c_M/[M]-1)K_{PY}/K_{MY}+1} \end{aligned} \tag{17}$$

and corresponding equations for [N] and [P]

$$\begin{aligned} f = \frac{[MY]}{c} + \frac{1}{(c_M/[MY]-1)}\,\frac{1}{cK_{MY}} + \frac{c_N}{c}\,\frac{1}{(c_M/[MY]-1)K_{MY}/K_{NY}+1} + \\ + \frac{c_P}{c}\,\frac{1}{(c_M/[MY]-1)K_{MY}/K_{PY}+1} \end{aligned} \tag{18}$$

and corresponding formulas for [NY] and [PY]

$$f = 1 + \frac{[Y]}{c} - \frac{c_M}{c}\,\frac{1}{[Y]K_{MY}+1} - \frac{c_N}{c}\,\frac{1}{[Y]K_{NY}+1} - \frac{c_P}{c}\,\frac{1}{[Y]K_{PY}+1} \tag{19}$$

The mathematical expressions for the titration curves of mixtures of metals are very similar to the titration curves of one metal M with a ligand Y, which can be derived directly or by putting $c_N = 0$ in eqns. (12), (14) and (15). The resulting formulae are:

$$f = 1 - \frac{[M]}{c} + \frac{1}{[M]K_{MY}} - \frac{1}{cK_{MY}} \tag{20}$$

$$f = 1 + \frac{[Y]}{c} - \frac{1}{[Y]K_{MY}+1} \tag{21}$$

$$f = \frac{[MY]}{c} + \frac{1}{(c/[MY]-1)}\,\frac{1}{cK_{MY}} \tag{22}$$

This mathematical similarity does not imply a similarity in the titration curves.

Graphical representation

The most convenient way to draw the titration curves is to divide f into several parts f_1, f_2, etc., drawing these parts separately and finally adding them graphically.

Examples can be based on the f–[M] equation for the titration of two metals M and N with one ligand, given by

$$f = 1 - \frac{[M]}{c} + \frac{c_M}{c}\,\frac{1}{[M]K_{MY}} - \frac{c_N}{c}\,\frac{1}{(c_M/[M]-1)K_{NY}/K_{MY}+1} - \frac{1}{cK_{MY}} \qquad (12)$$

There are two different possibilities for plotting this equation which are of practical importance, *viz.* a f–[M] plot and a f–pM plot. The former is important, for example, in the case of amperometric and photometric end-point detection, whereas the latter is of importance in judging the possibilities for end-point detection by potentiometry or visual metallochromic indicators.

In the present examples, the f–pM graphs have been chosen. In the case of f–pM graphs the term $1/cK_{MY}$ in eqn. (12) can be neglected, because it is nearly zero in all cases which are of practical importance. The other terms in eqn. (12) are named f_1, f_2 and f_3 from left to right, so that:

$$f = 1 + f_1 + f_2 + f_3$$

In Fig. 1 the f–pHg plot is given for the titration of a solution containing 0.0008 *M* mercury(II) and 0.0008 *M* lead(II) with 0.02 *M* DTPA at pH 6.0 (acetate buffer).

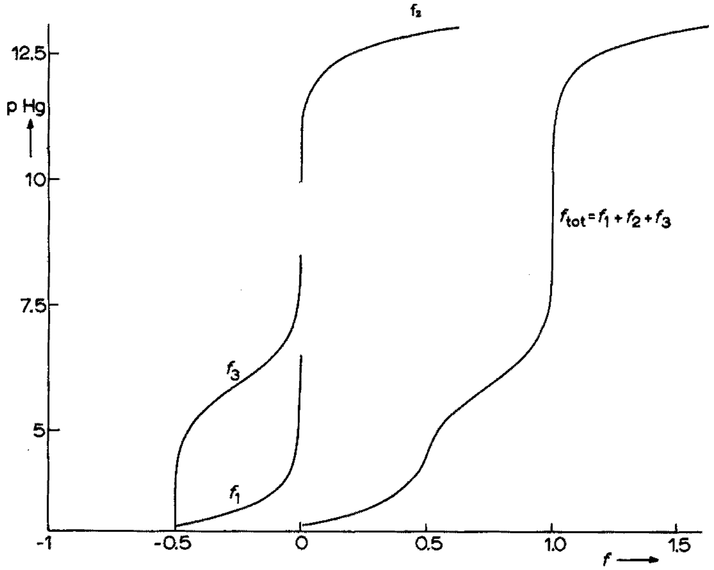

Fig. 1. Construction of the theoretical titration curve f–pHg for 0.0008 *M* Hg^{2+} and 0.0008 *M* Pb^{2+} in acetate buffer pH 6 with DTPA (0.02 *M*).

$$f = 1 + f_1 + f_2 + f_3;\ f_1 = -\frac{[Hg]}{c}$$

$$f_2 = \frac{c_{Hg}}{c}\,\frac{1}{[Hg]K_{Hg\,DTPA}};\ f_3 = -\frac{c_{Pb}}{c}\,\frac{1}{(c_{Hg}/[Hg]-1)K_{Pb\,DTPA}/K_{Hg\,DTPA}+1}$$

$\log K_{Hg\,DTPA} = 12.9$; $\log K_{Pb\,DTPA} = 10.1$.

The conditional stability constants used are $\log K_{Hg\,DTPA} = 12.9$ and $\log K_{Pb\,DTPA} = 10.1$. In Fig. 2 the same curve is drawn but pHg has been converted to mV *vs.* S.C.E.

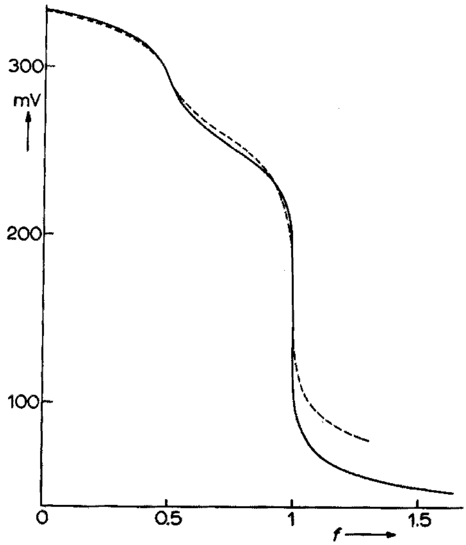

Fig. 2. Titration curves *f*-mV (mercury electrode *vs.* S.C.E.). —— Theoretical curve, calculated from Fig. 1 with log $\alpha_{Hg} = 6.5$. ---- Experimental curve, found with Radiometer automatic titrator (pH 6.0→5.9).

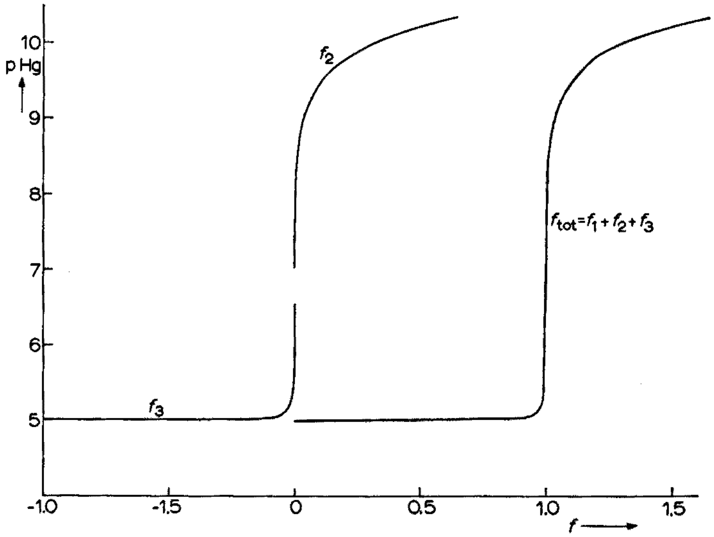

Fig. 3. Construction of the theoretical titration curve *f*-pHg for 0.1 *M* Cu^{2+} and 10^{-5} *M* Hg^{2+} in 2 *M* acetate buffer pH 5 with EDTA (0.4 *M*). log $K_{Hg\ EDTA} = 6.5$; log $K_{Cu\ EDTA} = 8.5$. In this case f_1 is omitted, because $f_1 < 10^{-3}$.

by means of the Nernst equation. The factor log $\alpha_{Hg} = 6.5$ is used to convert the conditional concentration of mercury to its actual concentration. Figure 2 also shows an experimental plot of this titration, as found with a Radiometer automatic titrator provided with a mercury electrode and S.C.E.*.

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* Full experimental details will be given in a subsequent paper.

Another example is the titration of a solution that contains 0.1 *M* copper(II) and 10^{-5} *M* mercury(II) with 0.4 *M* EDTA at pH 5.0 (acetate buffer). This solution corresponds to the conditions of the potentiometric determination of copper with a mercury indicator electrode. Figure 3 shows the theoretical *f*–pHg plot and Fig. 4 the theoretical as well as the experimental *f*–mV plot. The results show typical asymmetric curves which occur when $\log K_{MY} > \log K_{HgY}$. The conditional stability constants used in this second example were $\log K_{Hg\,EDTA} = 6.5$ and $\log K_{Cu\,EDTA} = 8.5$ whereas the conversion factor, $\log \alpha_{Hg}$, is 8.7 under these conditions.

The stability constants of the 4 complexes were calculated from values given by RINGBOM[5] and SILLÉN AND MARTELL[6].

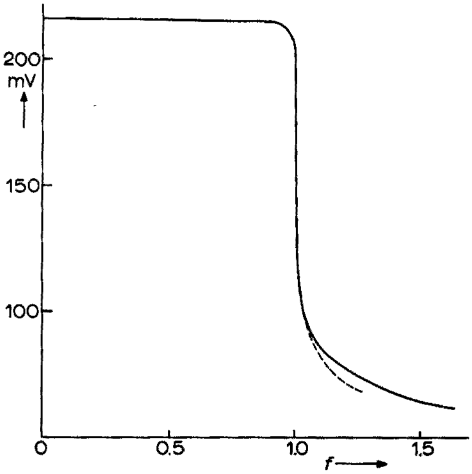

Fig. 4. Titration curves *f*–mV (mercury electrode *vs.* S.C.E.). —— Theoretical curve, calculated from Fig. 3 with $\log \alpha_{Hg} = 8.7$. ---- Experimental curve, found with Radiometer automatic titrator.

DISCUSSION

As already mentioned, the equations given in this paper are of practical importance for the selection of indication methods for the compleximetric titrations of mixtures of metals. In a following paper some general conclusions from *f*–pM graphs will be discussed, which are important for potentiometric and visual end-point detection.

SUMMARY

Formulae were calculated for the compleximetric titration of mixtures of two and of three metals with one ligand, giving the relation between a titration parameter *f* and the concentration of the metals, the ligand or the complexes separately.

RÉSUMÉ

Des expressions ont été calculées pour les courbes de titrage compleximétrique de mélanges de 2 et 3 métaux avec un agent complexant, donnant la relation entre un paramètre de titration *f* et la concentration des métaux, le réactif complexant ou les complexes, séparément.

ZUSAMMENFASSUNG

Für die Titrationskurven komplexometrischer Titrationen von 2 oder 3 Metallen nebeneinander, die nur einen Liganden besitzen, werden theoretische Ausdrücke abgeleitet. Die Ausdrücke ermöglichen eine einfache graphische Wiedergabe dieser Titrationskurven. An einigen Beispielen wird die Brauchbarkeit der Formeln erläutert.

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THE NEPHELOMETRIC DETERMINATION OF SMALL AMOUNTS OF SULPHATE ION

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The accurate determination of small amounts of sulphate is a matter of considerable importance in many branches of pure and applied chemistry and in many biochemical studies. Direct colorimetric procedures are few and not entirely satisfactory; reduction to hydrogen sulphide and its conversion to methylene blue is a sensitive process, but the many papers published on it testify to its basic unreliability. Methods based on the precipitation of barium sulphate (*e.g.* from barium chloranilate) are subject to the many interferences associated with this precipitation. Nevertheless, the barium ion remains the most widely used means for the determination of the sulphate ion, and many ingenious methods have been proposed, particularly for titrimetric and colorimetric purposes.

The rather low solubility of barium sulphate, particularly in mixed solvent systems of water and polyhydric alcohols has an obvious application in turbidimetry and nephelometry, and numerous such procedures are to be found in the literature. The basic method of DENIS AND REED[1] which deals with 1–10 p.p.m. of sulphate ion in a 25-ml sample has been modified by later workers; the method of TOENNIES AND BAKAY[2] is the most recent and thorough examination of this process.

Up to the present, little or no attention has been given to the replacement of barium by other precipitants for the sulphate ion in these nephelometric procedures. Benzidine is unfortunately less sensitive a precipitant for the sulphate ion than barium chloride, and substituted benzidines are, in general, even less sensitive, so that no advantage can accrue from the application of these reagents in turbidimetric or nephelometric procedures. However, the same cannot be said for one other precipitant for the sulphate ion, 4-amino-4′-chlorodiphenyl (trivially named CAD) which has found considerable application as a reagent for small quantities of sulphate by titrimetric[3] and spectrophotometric[4] methods. BELCHER AND STEPHEN[5] have indicated the superior sensitivity of this reagent to barium chloride, and state that it can detect by a precipitation reaction as little as 0.1 p.p.m. of sulphate ion in a volume of 50 ml. This sensitivity is about 10 times as great as that of the basic nephelometric method with barium chloride. The precipitate of CAD sulphate is extremely finely divided, and suspensions of this salt should be ideal for turbidimetric and nephelometric applications. HASLAM, HAMILTON AND SQUIRRELL[6] in an account of the detection of certain elements in plastic materials by the flask combustion method, recommend a turbidimetric CAD hydrochloride method as an alternative to the standard barium chloride method for the detection and semiquantitative determination of sulphur in the test material. The suspension of CAD sulphate is stabilised by the presence of gum ghatti and peptone in the reagent solutions, and the optical density of the suspension is measured at 700 nm after 0.5 h. Only semiquantitative applications are proposed for amounts of sulphur of the order 1–2% in the test material. These workers do, however, emphasise the sensitivity of the CAD hydrochloride reagent and recommend its use when only trace amounts of sulphur are to be detected.

Nephelometric procedures are generally more sensitive than comparable turbidimetric procedures in which the concentration of a suspension is measured by diminution of incident light. In nephelometry, the light scattered by the particles of the suspension is measured directly at an angle (usually 90°) to the incident beam. Various types of nephelometer are available commercially in which almost all the scattered light from just above 0° to 90° from the incident beam is collected and measured. Such instruments enable less stringent conditions to be placed on requirements of particle size, which for purposes of maximal scattering should be about 0.2–0.4 μ. Smaller particles scatter less intensely, but evenly in all directions; larger particles also scatter less intensely but mainly within 10° from the incident beam. Although the intensity of light scattered at a given angle is dependent on the size and shape of the suspended particles, on the wavelength of the incident light and on the ratio of the refractive indices of the particle and the medium in which it is suspended, as well as on its concentration, particle size is the most significant variable in any analytical procedure involving nephelometric measurements[7]; the reproducible formation of similarly sized particles is the prerequisite for successful nephelometric determinations.

In the present investigation, conditions have been established for the determination of 0.025–0.25 mg of sulphate in 10-ml volumes of test solution (*i.e.* concentrations of 2.5–25 p.p.m. of sulphate) by nephelometric measurement of CAD sulphate suspensions, stabilised with gum ghatti.

A study of the effect of other anionic species on the determination has shown that chloride and nitrate ions present in concentrations 10 times that of the maximal sulphate concentration are without effect. Fluoride and phosphate ions are known to interfere with the recommended titrimetric method for sulphate using CAD hydrochloride and these ions would be expected to cause a similar interference in the nephelometric method. A 10-fold concentration of fluoride ion (*i.e.* 2.5 mg F^-/10 ml) gives a curdy gelatinous precipitate with the CAD reagent, which disappears when the concentration is reduced to about 1.8 mg of fluoride. However, in the presence of this amount of fluoride ion, the apparent sulphate content is considerably higher than that actually present, and only when the fluoride concentration is reduced to 0.25 mg does this interference disappear. With phosphate, the CAD reagent forms precipitates with concentrations below 0.25 mg of $H_2PO_4^-$ in 10-ml volumes and it is necessary to remove phosphate ions from the test sample by treatment with magnesia mixture. A procedure which deals with phosphate in amounts up to 2.5 mg of $H_2PO_4^-$ in 10 ml of test sample has been developed to overcome this interference. No other anionic species has been examined as a possible interference, but it is known that bromide and iodide ions, and the organic acids, acetic, citric and tartaric acids, are without effect on the precipitation of sulphate ions by CAD hydrochloride[3]. Cationic interferences have not been examined in the present investigation. Of the common cations, only aluminium is known to form a sparingly soluble complex salt with the reagent in neutral solutions containing sulphate ions; zinc, copper and magnesium form soluble complexes with the reagent, but should not interfere when present in 10-fold amounts. If high concentrations of cations (other than the alkali metals) were present in the test solution, these could be conveniently removed by an ion-exchange resin, and the resulting acid test solution neutralised before application of the nephelometric procedure.

EXPERIMENTAL

Apparatus

Nephelometric measurements were made with the EEL Nephelometer Head in conjunction with the EEL Unigalvo Type 20. Test tubes ($\frac{3}{4}''$ diam., volume *ca.* 25 ml) provided with the instrument were used to contain the suspensions.

Reagents

CAD hydrochloride solution (Solution A). Dissolve 2.0 g of 4-amino-4′-chlorodiphenyl hydrochloride[3] in 800 ml of hot (70°) 0.05 *N* hydrochloric acid. Cool the solution and filter through a Whatman No. 40 paper. If the solution is to be stored for prolonged periods, dark bottles should be used.

CAD hydrochloride–peptone solution (Solution B). Dissolve 0.025 g of biological reagent grade peptone in 50 ml of solution A by warming to 70°. Cool and filter through 2 Whatman No. 40 papers. Prepare this solution daily.

Gum ghatti solution. Dissolve 0.5 g of finely ground gum ghatti in 200 ml of 0.05 *N* hydrochloric acid by warming to 70°. Cool the solution and filter off undissolved material on double Whatman No. 40 papers. Store the solution at 0–5° and discard at the first signs of the formation of small particles in the solution.

Composite precipitation reagent (Solution C). Mix 10 ml of solution B and 90 ml of solution A shortly before use.

Potassium sulphate solution (0.025 mg sulphate per ml). Dissolve 0.0454 g of freshly dried A.R. potassium sulphate in 1 litre of water.

Magnesia mixture. Dissolve 20 g of A.R. ammonium chloride and 10 g of A.R. magnesium chloride hexahydrate in 100 ml of water.

Procedure

Neutral test solutions (phosphate absent). To 10 ml of the neutral test solution, contained in a 50-ml stoppered flask (volumetric flasks are convenient, but not essential), add 12 ml of the composite reagent, solution C. After 15 sec, stopper the flask, swirl the contents for a further 15 sec and invert the flask once per second for 30 sec. Leave for 45 min and then add with gentle swirling, 3 ml of gum ghatti solution. After a further 15 min, transfer the whole of the suspension to one of the nephelometer tubes (*Note*), taking care to avoid formation of air bubbles in the suspension; measure its effective light scattering power in the nephelometer, previously adjusted to give maximal galvanometer deflection (100) with the most concentrated standard suspension (0.25 mg of sulphate per 10 ml) and zero deflection on distilled water. Prepare a calibration graph for amounts of sulphate ion in the range 0.025–0.25 mg per 10 ml of standard solution and determine the sulphate content of the test solutions from the standard graph. A blank determination should be included in each series of calibrations.

Note. The nephelometer tubes should be thoroughly cleaned periodically in chromic–sulphuric acid solution to minimise the risk of air bubbles forming on the walls of tubes when the suspensions are poured into them.

Acid test solutions. To 10 ml of the test solution contained in a 25-ml beaker, add 0.3 ml of ammonia solution (d. 0.88), and carefully evaporate the solution to a volume of 3–5 ml. Transfer the solution to a 10-ml measuring cylinder and rinse the beaker with small amounts of water to give a volume of 7 ml in the measuring cylinder. Transfer this volume of solution to the 50-ml precipitation vessel and rinse the beaker and the cylinder with 2 ml of water, made up to 3 ml in the cylinder; add this 3 ml to the 7 ml in the precipitation vessel. Precipitate the sulphate as described above. Treat the standards in the same way to compensate for the traces of sulphate present in the additional reagents.

Phosphate present. To 15 ml of test solution, containing 2.5–25 p.p.m. of sulphate, add 0.1 ml of 4 N hydrochloric acid, 0.6 ml of magnesia mixture and 0.3 ml of ammonia solution (d. 0.88). Mix well and store overnight at 0°. Centrifuge the precipitated magnesium ammonium phosphate and pipette 10 ml of the clear supernatant liquid into a 25-ml beaker. Remove excess of ammonia by boiling and make up the volume to 10 ml as described under *Acid test solutions.* Prepare standards from 10-ml aliquots of sulphate solution, treated with identical amounts of the phosphate-precipitating reagents, and adjust the volumes to 10 ml as described above. Determine the amount of sulphate in the test solution from the calibration graph and multiply the result by the volume correction factor, 1.067.

RESULTS AND DISCUSSION

The analytical procedure is designed to deal with 10-ml test samples containing sulphate ion at concentrations in the range 2.5 to 25 p.p.m. It can be extended to slightly higher concentrations (30 p.p.m.) without impairment of accuracy. The results in Table I are typical, and show an average error of ±2.8%. Comparison of the new method with the standard barium sulphate method[8] indicates that the CAD method is considerably more sensitive and capable of dealing with a smaller total amount of sulphate in the test solution.

TABLE I

RESULTS BY THE RECOMMENDED PROCEDURE

(Volume of test sample: 10 ml)

Sulphate present (p.p.m.)	*Sulphate found (p.p.m.)*	*Error (%)*	*Sulphate present (p.p.m.)*	*Sulphate found (p.p.m.)*	*Error (%)*
30.0	30.5	+ 1.7	15.0	15.5	+ 3.3
24.0	24.5	+ 2.1	12.0	12.0	0.0
22.5	22.0	− 2.3	10.0	9.8	− 2.0
18.0	16.8	− 6.7	8.5	8.0	− 5.9
16.5	16.5	0.0	5.0	4.9	− 2.0
15.8	16.2	+ 2.5			

No difficulty is experienced in obtaining linear calibration graphs by the recommended procedure. The line need not pass through the origin; its intercept on the axis of the galvanometer readings is generally small (between 2 and 5%) and is obtained from the measurement of the blank solutions. The small variation in the blank values depends largely on the age of the reagents, in particular, that of the gum ghatti solution. The properties of this solution change slightly from day to day, despite storage of the solution in a refrigerator, so that no two standard graphs are exactly the same, unless constructed on the same day. It is, therefore, essential that tests and standards are prepared as nearly as possible under identical conditions, certainly with the same reagents, and on the same day. Alternative forms of the gum ghatti solution, and indeed, alternative stabilisers such as gum acacia, gave rise to very inferior results, and the procedure described above was established only after considerable variation of the conditions for the preparation of stable suspensions.

When sulphate–phosphate solutions were examined, the results indicated that a constant increment of 2 p.p.m. of sulphate was present in each sample. Experiments with solutions containing standard amounts of sulphate, and no phosphate, but with the addition of the requisite amounts of reagents necessary to remove the phosphate ion also gave consistently high results, indicating that the reagents contained appreciable amounts of sulphate ion as impurity (Fig. 1). It is, therefore, essential to treat standard samples in exactly the same way as the test solutions; under these conditions, it is possible to determine sulphate in the presence of up to 25 p.p.m. of $H_2PO_4^-$ without any loss of precision.

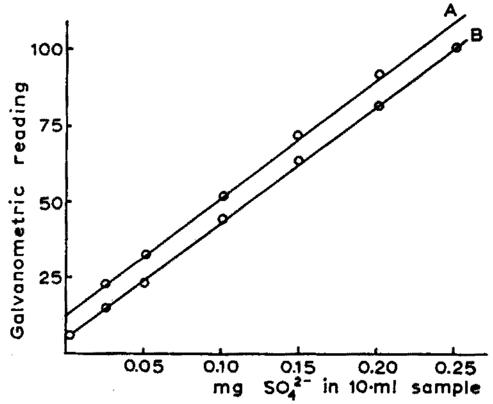

Fig. 1. Typical calibration graphs. (A) Samples from which 0.25 mg $H_2PO_4^-$ was precipitated; (B) standard sulphate solutions.

The new method should find application for the determination of traces of sulphate ion in water samples, or of sulphur in organic and biological materials after conversion to sulphate ion.

Because of the known carcinogenicity of benzidine and 4-aminodiphenyl, doubts have been cast on 4-amino-4′-chlorodiphenyl as a possible carcinogen. Physiological studies with rats have shown that this compound has no significant properties as a carcinogen, compared with the parent amine and the 4-fluoro-derivative[9]; its use as an analytical reagent should not be restricted on this account.

We are grateful to Professor R. Belcher for his interest in this work, Dr. F. L. Rose (I.C.I. Pharmaceuticals Division) for his comments on the carcinogenicity of the reagent and the University of Birmingham for financial support to J.M.M.

SUMMARY

A method is proposed for the nephelometric determination of the sulphate ion in concentrations of 2.5–25 p.p.m. in test volumes of 10 ml. The sulphate is precipitated with a solution of 4-amino-4′-chlorodiphenyl hydrochloride, and the resultant suspension of amine sulphate is stabilised with gum ghatti. Phosphate ions interfere and are removed as magnesium ammonium phosphate beforehand. Fluoride ion up to 25 p.p.m. has no effect on the determination.

RÉSUMÉ

On propose une méthode pour le dosage néphélométrique des sulfates (2.5 à 25 p.p.m./10 ml). On précipite le sulfate à l'aide de chlorhydrate d'amino-4-chloro-4′-diphényle. Les ions phosphates gênent et doivent être éliminés au préalable sous forme de phosphate ammoniacomagnésien. Les ions fluorures jusqu'à 25 p.p.m. ne gênent pas.

ZUSAMMENFASSUNG

Es wird eine Methode vorgeschlagen zur nephelometrischen Bestimmung des Sulfations für Konzentrationen zwischen 2.5 und 25 p.p.m. in einem Volumen von 10 ml. Das Sulfat wird mit einer Lösung von 4-Amino-4′-chlorodiphenylhydrochlorid gefällt und die resultierende Suspension mit Gummighatti stabilisiert. Phosphationen stören und werden vorweg als Magnesiumammoniumphosphat abgeschieden. Fluorionen bis zu 25 p.p.m. beeinflussen die Bestimmung nicht.

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ETUDE THERMOMETRIQUE DE LA FORMATION DES COMPLEXES DU FER(III), DE L'ALUMINIUM ET DU GALLIUM

I. OXALATES ET MALONATES

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(Reçu le 27 mars, 1967)

Des travaux déjà anciens[1] avaient montré qu'on pouvait suivre la formation d'un complexe métallique par voie thermométrique mais les appareillages rudimentaires alors utilisés étaient trop peu sensibles pour révéler vraiment l'intérêt de cette technique. Grâce aux dispositifs à thermistances qui se sont répandus depuis quelques années, la thermométrie est en passe de donner toute sa mesure, s'avérant parfaitement comparable et dans certains cas même plus féconde que les méthodes physicochimiques classiques lorsqu'il s'agit de suivre les étapes d'une réaction.

Nous nous proposons de montrer avec quelle facilité et quelle rapidité on peut mettre en évidence par voie thermométrique la formation successive d'une série de complexes solubles dans un système cation–coordinat. Ayant choisi, pour illustrer l'emploi de cette technique, le cas des oxalates, malonates, tartrates et citrates de cations tripositifs (Al^{3+}, Fe^{3+} et Ga^{3+}) nous constaterons que l'on peut, souvent à l'aide d'un seul enthalpogramme, confirmer l'existence des complexes déjà signalés et éventuellement en caractériser de nouveaux. Il convient cependant de préciser, par quelques remarques préliminaires comment il y a lieu d'opérer pour tirer le maximum de profit d'une telle méthode.

Lorsqu'un coordinat anionique L^{n-} ($n \geqslant 0$) se fixe sur un cation M^{m+} de coordinence N, on assiste en général à la formation de complexes successifs correspondant à des rapports métal/coordinat décroissants.

	rapport $r = [M]/[L]$
$M^{m+} + L^{n-} \rightleftarrows [ML]^{m-n}$	1:1
$[ML]^{m-n} + L^{n-} \rightleftarrows [ML_2]^{m-2n}$	1:2
$[ML_{N-1}]^{m-(N-1)n} + L^{n-} \rightleftharpoons [ML_N]^{m-nN}$	1:N

La constante de stabilité du *x*ième complexe de la série étant définie (en confondant activité et concentration) par l'expression

$$K_x = \frac{[ML_x]}{[ML_{x-1}][L]} \qquad \text{(en négligeant les charges des espèces)}$$

on voit que si $K_{x-1} < K_x < K_{x+1}$, c'est à dire si les complexes successifs sont de stabilité décroissante, on aura avantage à ajouter progressivement le coordinat à l'ion métallique pour former d'abord le complexe le moins stable ML_{x-1} puis les suivants. Si au contraire $K_{x-1} > K_x > K_{x+1}$, c'est à dire si la stabilité des complexes successifs décroît, il conviendra d'ajouter l'ion métallique à la solution de coordinat pour former d'abord ML_{x+1} et ensuite les suivants.

D'autre part, la concentration [L] du coordinat qui est en fait celle des anions L^{n-} est déterminée par la constante d'acidité de l'acide organique H_nL et le pH du milieu. Ce dernier est effectivement d'importance capitale car chaque complexe se formera généralement dans sa zone particulière de pH et lorsqu'on voudra suivre la formation successive des complexes d'une série, il conviendra de réaliser un gradient de pH dans le sens convenable, tout au long de l'addition de réactif.

APPAREILLAGE ET MODE OPÉRATOIRE

L'appareil utilisé était un thermotitrimètre de construction "SOLYREG" déjà décrit dans 2 publications[2,3]. Il comporte essentiellement 2 thermistances identiques, plongeant chacune dans un bac de verre contenant le réactif à doser et placé lui-même dans un vase Dewar calorifugé. Une burette automatique introduit à vitesse constante le titrant dans l'un des bacs; les thermistances constituant 2 des branches d'un pont de Wheatstone, le déséquilibre de celui-ci, qui résulte de l'effet thermique de la réaction agissant sur l'une des thermistances, est enregistré sur un potentiomètre MECI.

Pour réaliser une expérience, c'est à dire enregistrer un enthalpogramme, on opère de la façon suivante: Dans chacun des bacs du thermotitrimètre, on introduit: (*a*) un volume connu de solution titrée du cation à complexer ou du coordinat; (*b*) un volume constant de solution concentrée d'un sel (KNO_3) servant à fixer à une valeur suffisante la force ionique du milieu, (*c*) une base ou un acide servant à ajuster le pH initial à la valeur exigée pour la formation du premier complexe de la série; (*d*) la quantité d'eau distillée nécessaire à amener le volume de cette solution à 80–90 ml. L'agitation est mise en route simultanément dans les 2 bacs (agitateurs tournant à la même vitesse) et dès que l'équilibre de température est obtenu, on introduit dans l'un des bacs, par un tube effilé relié à la burette automatique, le réactif de complexation (coordinat ou cation) amené lui-même au pH convenable pour réaliser le gradient de pH optimal durant cette addition progressive.

Pour toutes les courbes enregistrées on a utilisé le même débit de la burette automatique soit 0.3101 ml/min et la même vitesse de déroulement du papier de l'enregistreur (15.24 mm/min). Il défilait donc 49.17 mm de papier pour chaque ml de réactif ajouté. Pour obtenir dans chaque cas l'enthalpogramme le plus exploitable, il a fallu choisir convenablement la tension d'alimentation du pont de mesure (0–3 V) et la sensibilité de l'enregistreur (1 à 25 mV).

COMPLEXES OXALIQUES

De l'abondante littérature consacrée aux complexes oxaliques exposée jusqu'en 1960 dans un article d'ensemble exhaustif[4] et que nous avons complété pour les années plus récentes, nous ne retiendrons, en raison de leur intérêt pour notre travail que l'étude thermométrique des oxalato thorates[5] et la détermination, par la méthode, statistique de BJERRUM, des constantes de stabilité des complexes trisoxaliques (et maloniques) du Cr(III), Fe(III), Al(III), Ga(III)[6]. Ces travaux concluent à l'existence de

3 complexes oxaliques pour ces métaux, correspondant aux rapports $r = 1:1$, $1:2$ et $1:3$ respectivement et de constantes de stabilité décroissantes ($K_1 > K_2 > K_3$).

Complexes oxaliques de l'aluminium(III)

Pour les raisons précédemment exposées, nous avons ajouté une solution d'aluminium (à faible pH) à un oxalate (à pH plus élevé) de façon à former d'abord le complexe 1:3 (le moins stable) et à former ensuite les autres à pH décroissant. Conditions opératoires: Dans les bacs thermométriques: solution $K_2C_2O_4$ 1.3518 *M* à pH 7 + KNO_3. Dans la burette: solution $Al(NO_3)_3$ 1.0080 *M* à pH 2. Tension d'alimentation du pont: 1.5 V. Sensibilité de l'enregistreur: 2.5 mV. Les enthalpogrammes enregistrés ont la forme de la Fig. 1 et les résultats obtenus pour les 4 concentrations étudiées sont rassemblés sur le Tableau I.

Dans ce Tableau et dans tous les suivants:
Vol. prise d'essai: quantité de solution placée dans chacun des bacs thermométriques.
r : rapport métal/coordinat.
l(mm) : longueur des abscisses des brisures (l exp désignant la moyenne de la longueur mesurée pour 2 essais successifs).
Δ : différence entre la théorie et l'expérience.

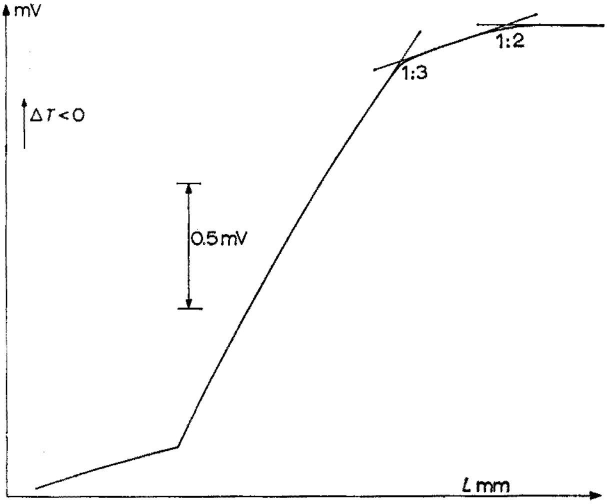

Fig. 1. Oxalates d'aluminium.

TABLEAU I

COMPLEXES OXALIQUES DE L'ALUMINIUM(III)

l(mm) / *r*	*Vol. prise d'essai*											
	1.25 ml			*2.5 ml*			*3.75 ml*			*5 ml*		
	Théor.	*Exp.*	*Δ (%)*	*Théor.*	*Exp.*	*Δ (%)*	*Théor.*	*Exp.*	*Δ (%)*	*Théor.*	*Exp.*	*Δ (%)*
1:3	28.5	29	+1.5	57	57	0	85.5	85	0.6	114	113	−1
1:2	43	44	+2	86	87.5	+2	129	128.5	−0.5	171	172.5	+1

Nous pouvons conclure que, dans nos conditions expérimentales, nous mettons en évidence exclusivement les *complexes 1:3 et 1:2*. Ces rapports sont déterminés sans ambiguité puisque l'écart maximal entre les abscisses théoriques et lues sur l'enthalpogramme ne dépasse pas 2% et qu'en représentant les abscisses lues en fonction des volumes de la prise d'essai, on obtient d'excellentes droites de proportionnalité (non représentées ici) et passant par l'origine des coordonnées.

Complexes oxaliques du fer(III)

Nous avons opéré dans des conditions très semblables à celles du paragraphe précédent mais nous avions intérêt à choisir un milieu plus acide pour tenir compte des zônes de formation indiquées par BABKO ET DUBOVENKO[7] pour les 3 complexes qu'il a caractérisés, respectivement: $\text{pH} > 2.5$ pour le complexe 1:3; $1 < \text{pH} < 2.5$ pour le complexe 1:2; et $\text{pH} < 1$ pour le complexe 1:1.

Conditions opératoires: Dans les bacs thermométriques: solution $K_2C_2O_4$ 1.3518 M à pH 6 + KNO_3. Dans la burette: solution $Fe(NO_3)_3$ 2.0071 M à $\text{pH} < 1$. Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 2.5 mV. Les

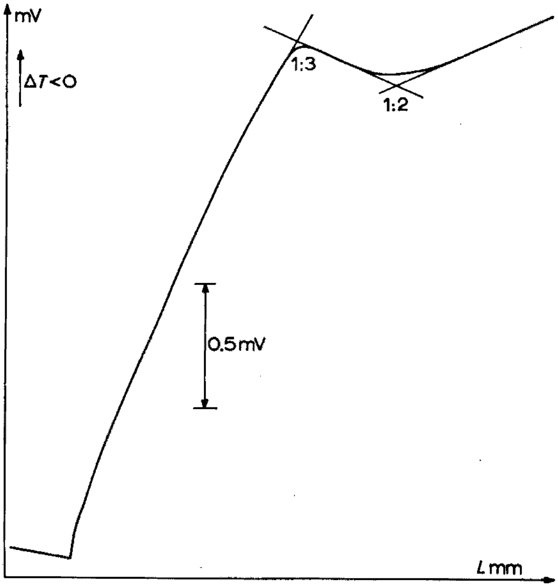

Fig. 2. Oxalates de fer(III).

TABLEAU II

COMPLEXES OXALIQUES DU FER(III)

r \ l(mm)	Vol. prise d'essai								
	2.5 ml			5 ml			7.5 ml		
	Théor.	*Exp.*	*Δ(%)*	*Théor.*	*Exp.*	*Δ(%)*	*Théor.*	*Exp.*	*Δ(%)*
1:3	28.5	28.25	−1	57	57	0	85.5	86	+0.75
1:2	43	43.5	+1	86	84.5	−2	129	127.5	−1

enthalpogrammes enregistrés ont la forme de la Fig. 2 et les résultats obtenus pour les 3 concentrations étudiées sont rassemblés sur le Tableau II.

Nous concluons que, dans nos conditions expérimentales, nous mettons encore ici en évidence exclusivement les complexes 1:3 et 1:2, comme dans le cas de l'aluminium. Ces rapports sont déterminés sans ambiguité puisque l'écart maximal entre les abscisses théoriques et les abscisses lues sur l'enthalpogramme ne dépasse pas 2% et qu'en représentant ces abscisses lues en fonction des volumes de la prise d'essai, on obtient d'excellentes droites de proportionnalité passant par l'origine.

Remarque. Surpris de ne pouvoir confirmer l'existence des complexes 1:1 dans le cas fer et de l'aluminium, nous avons essayé d'inverser l'ordre d'addition des réactifs, en versant la solution d'oxalate dans la solution du cation. Les enthalpogrammes obtenus ainsi ne présentent plus aucun changement d'allure. Nous sommes donc obligés de conclure que le complexe 1:1, s'il existe comme cela est vraisemblable d'après les travaux antérieurs, est très difficile à déceler par thermométrie.

COMPLEXES MALONIQUES

Beaucoup moins étudiés que les oxalates, les complexes maloniques des cations tripositifs font l'objet de quelques publications[8-12] signalant en général l'existence

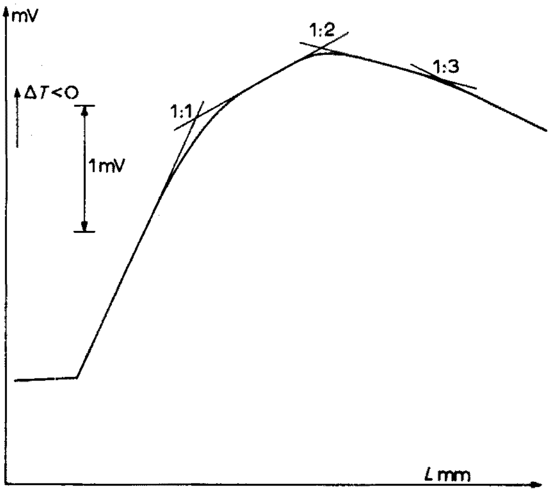

Fig. 3. Malonates d'aluminium.

BLEAU III

MPLEXES MALONIQUES DE L'ALUMINIUM(III)

l(mm)	Vol. prise d'essai											
	2 ml			3 ml			4 ml			5 ml		
	Théor.	Exp.	Δ(%)	Théor.	Exp.	Δ(%)	Théor.	Exp.	Δ(%)	Théor.	Exp.	Δ(%)
	32.5	33	1.5	49	49	0	65	64.5	1	81.5	81.25	0.3
	65	64.75	0.4	98	98.25	0.3	130	129	1	162	161.25	0.5
	97.5	97.5	0	147	147.5	0.3	195	194.5	0.3	243	242.25	0.3

de 3 complexes correspondant, comme pour les oxalates, aux rapports 1:1, 1:2 et 1:3 mais, à l'inverse des oxalates, leurs constantes de stabilité sont croissantes $(K_1 < K_2 < K_3)$. Pour caractériser leur formation successive par voie thermométrique, il conviendra donc d'ajouter une solution d'ions malonate à la solution du cation de façon à former d'abord le complexe 1:1, puis les suivants, à pH croissant.

Complexes maloniques de l'aluminium(III)

Conditions opératoires: Dans les bacs thermométriques: solution $Al(NO_3)_3$ 1.0012 *M* à pH 4+KNO_3. Dans la burette: solution 3.002 *M* d'acide malonique neutralisé jusqu'à pH 6.5 par NH_4OH. Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 5 mV. Les enthalpogrammes enregistrés ont la forme de la Fig. 3 et les résultats obtenus pour les 4 concentrations étudiées sont rassemblées sur le Tableau III.

Bien que les diverses branches des enthalpogrammes se raccordent suivant des arcs de courbe révélant le caractère équilibré des réactions successives considérées, il est cependant possible par extrapolation des segments de droite de fixer avec une très bonne précision les rapports correspondant aux 3 complexes. On retrouve bien par thermométrie les trois rapports 1:1, 1:2 et 1:3 signalés dans la littérature[10,12] et en représentant les abscisses lues sur les enthalpogrammes en fonction des volumes de prises d'essai, on obtient d'excellentes droites de proportionnalité.

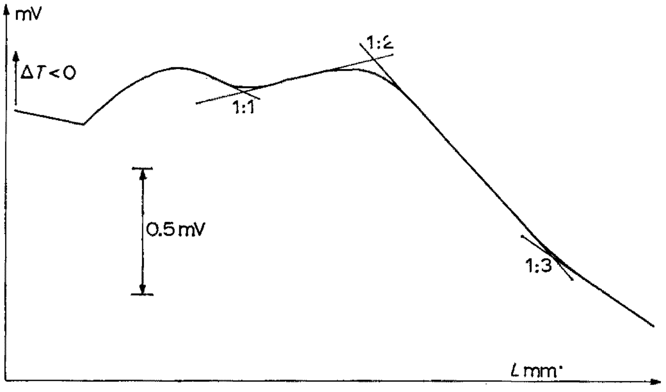

Fig. 4. Malonates de fer(III).

TABLEAU IV

COMPLEXES MALONIQUES DU FER(III)

l(mm)	*Vol. prise d'essai* 2 ml			3 ml			4 ml			5 ml		
	Théor.	*Exp.*	*Δ(%)*	*Théor.*	*Exp.*	*Δ(%)*	*Théor.*	*Exp.*	*Δ(%)*	*Théor.*	*Exp.*	*Δ(%)*
1:1	30	30	0	45	44.5	1	60	61	1.5	75	74	1.5
1:2	60	58.75	3	90	87.5	2.5	120	117	3	150	146.5	3
1:3	90	91.5	1.5	135	135	0	180	183	1.5	225	221	2

Complexes maloniques du fer(III)

Conditions opératoires: Dans les bacs thermométriques: solution 1.005 *M* $Fe(NO_3)_3$ à pH 2 + KNO_3. Dans la burette: solution 3.304 *M* d'acide malonique neutralisé jusqu'à pH 5 par NH_4OH. Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 2.5 mV. Les enthalpogrammes enregistrés ont la forme de la Fig.4 et les résultats obtenus pour les 4 concentrations étudiées sont rassemblés dans le Tableau IV.

Bien que la littérature ne fournisse que très peu de renseignements sur les complexes maloniques du Fe(III) on pouvait s'attendre à retrouver des espèces semblables aux oxalates d'aluminium. Effectivement nos résultats montrent que les complexes 1:1, 1:2 et 1:3 se forment successivement; bien que la brisure correspondant à la formation du second soit décalée en moyenne de 3%, celle-ci est cependant très nette et aucun doute n'est possible sur l'existence de ce complexe et sur sa formule.

Complexes maloniques du gallium(III)

Conditions opératoires: dans les bacs thermométriques: solution de $GaCl_3$ 0.3041 *M* à pH 2 + KNO_3. Dans la burette: solution 2.721 *M* d'acide malonique neutralisé à pH 6 par NH_4OH. Tension d'alimentation du pont: 2 V. Sensibilité de l'enregistreur: 2.5 mV.

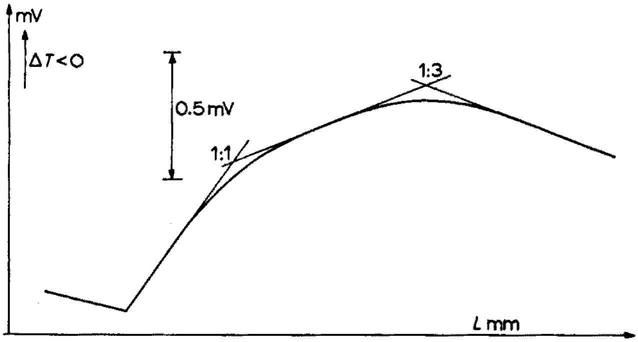

Fig. 5. Malonates de gallium(III).

Les enthalpogrammes enregistrés ont la forme de la Fig. 5 où l'on remarque de faibles portions rectilignes reliées par des arcs de courbe importants qui ne permettent de localiser avec précision les étapes de la réaction. D'une série de résultats assez dispersés nous avons cependant pû conclure que les complexes 1:1 et 1:3 sont très vraisemblables mais que la thermométrie n'apporte aucune preuve à l'existence de l'espèce intermédiaire 1:2.

CONCLUSIONS

Les résultats exposés ci-dessus illustrent l'intérêt de la méthode thermométrique pour caractériser de façon rapide, par l'enregistrement d'un seul enthalpogramme, la formation des divers complexes que forment les ions tripositifs avec les anions oxalate ou malonate.

Dans le cas des oxalates d'aluminium et de fer, la méthode thermométrique ne confirme que les complexes 1:2 et 1:3 parmi les 3 que signalent les références bibliographiques. Par contre, pour les malonates de fer et d'aluminium, les trois complexes 1:1, 1:2 et 1:3 déjà connus peuvent être retrouvés par thermométrie. Enfin cette dernière méthode permet d'admettre seulement l'existence des malonates de gallium 1:1 et 1:3.

RÉSUMÉ

On décrit un appareillage et un mode opératoire pour la détection thermométrique de la formation successive des complexes oxaliques et maloniques de cations trivalents. Les trois malonates de fer et d'aluminium sont retrouvés par cette méthode, mais seulement deux des trois oxalates ont pu être mis en évidence.

SUMMARY

Apparatus and experimental techniques are described for the thermometric detection of the stepwise formation of trivalent cation complexes with oxalate and malonate anions. The three iron and aluminium malonates were confirmed by this method but only two of the three oxalates could be found.

ZUSAMMENFASSUNG

Es wird eine Apparatur und die experimentelle Technik beschrieben, mit der die stufenweise Bildung von Oxalato- und Malonato-Komplexen 3-wertiger Kationen thermometrisch nachgewiesen wird. Die drei Eisen- und Aluminium-Malonate wurden mit Hilfe dieser Technik erneut bestätigt, während nur 2 der drei Oxalate gefunden werden konnten.

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THE REACTION BETWEEN PALLADIUM(II) AND COMPLEXES OF 8-QUINOLINOL-5-SULFONIC ACID

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In previous work[1], the fluorescent magnesium(II) complex of 8-quinolinol-5-sulfonic acid was used as a titrant, and unsatisfactory results were obtained when palladium(II) was titrated. Since the stability constants of palladium(II) complexes are usually of the same order of magnitude as those of copper(II) or nickel(II) complexes[2], the reaction with palladium(II) was investigated further.

EXPERIMENTAL

Chemicals

8-Quinolinol-5-sulfonic acid (Eastman Kodak Co.) was used without further purification. Palladium chloride was obtained from A. D. Mackay Co., New York. Other salts were reagent-grade hydrated sulfates.

Approximately $10^{-3}\,M$ solutions were prepared from more concentrated solutions. With the exception of copper(II) sulfate pentahydrate, salt solutions were standardized against EDTA, which had been standardized against the copper(II) sulfate, which was taken as the ultimate standard for all solutions.

The titrants used were solutions containing 8-quinolinol-5-sulfonic acid complexed with magnesium(II), cadmium(II) and zinc(II) in a ligand–metal ion ratio of 2:1 at a pH of 7.

Titration method

The spectral emission maxima (obtained with a Farrand spectrofluorimeter) for the titrants are all between 510 and 525 nm. In this investigation, a Turner Model 110 fluorimeter was used, with filter 811 in the primary beam, and a combination of 816 and 125 in the secondary beam, to transmit green light. It was found possible to extend the scale by rebalancing the instrument to zero when readings approached 100, adding subsequent readings to those obtained before the adjustment. Titration results were obtained by pipetting a given volume of cation into 200 ml of buffer pH 7. The fluorimeter was set to zero by rinsing some of this solution back and forth between the beaker and the small test tube used for making the fluorescence measurements, putting the test tube containing some of the solution in place in the instrument and balancing the scale to zero. The titrant was added in small increments from a McCloskey buret, the solution mixed well and the transfer (with mixing) to the test tube repeated. Any fluorescence was measured by rebalancing. Titrant was added until there was a constant increase in fluorescence per ml of titrant added. The use of a large starting volume has the effect of minimizing dilution errors. It also produced concentrations of the fluorescing complex in the neighborhood of 10^{-5} M, which decreased any error due to self-absorption of the emitted light by the fluorescing solution.

The above procedure works well for most bivalent cations[1], but not for palladium(II). To carry out the titrations and determine palladium(II), it was necessary to add an excess of titrant, heat the solution to boiling, and hold it near boiling for about 10 min. The solution was then cooled to room temperature and its fluorescence remeasured. The titration was then continued until another straight line was obtained. (Figs. 1–3)

Rate studies were made by rapid mixing of palladium(II) solutions with solutions of the fluorescent ZnL_2^{2-} complex. Fluorescence measurements were made at intervals, starting immediately after mixing. (Fig. 4)

The results shown in Fig. 5 were obtained by mixing, in 50-ml beakers, varying amounts of ZnL_2^{2-} with a fixed amount of palladium(II) solution, contained in 10 ml of a phosphate buffer of pH 7. These solutions were heated to boiling, cooled, washed into 100-ml volumetric flasks, and made up to volume. The palladium(II) and ZnL_2^{2-} solutions had both been diluted to 10^{-4} M before being mixed, so that the final concentrations after the final dilution were in the neighborhood of 10^{-6} M.

DISCUSSION OF RESULTS

Consideration of the titration curves shown in Figs. 1–3 shows that the anomalous results previously reported[1] for the titration of palladium(II) with fluorescent complexes of 8-quinolinol-5-sulfonic acid are due to a slow reaction between palladium(II) and the complex.

TABLE I

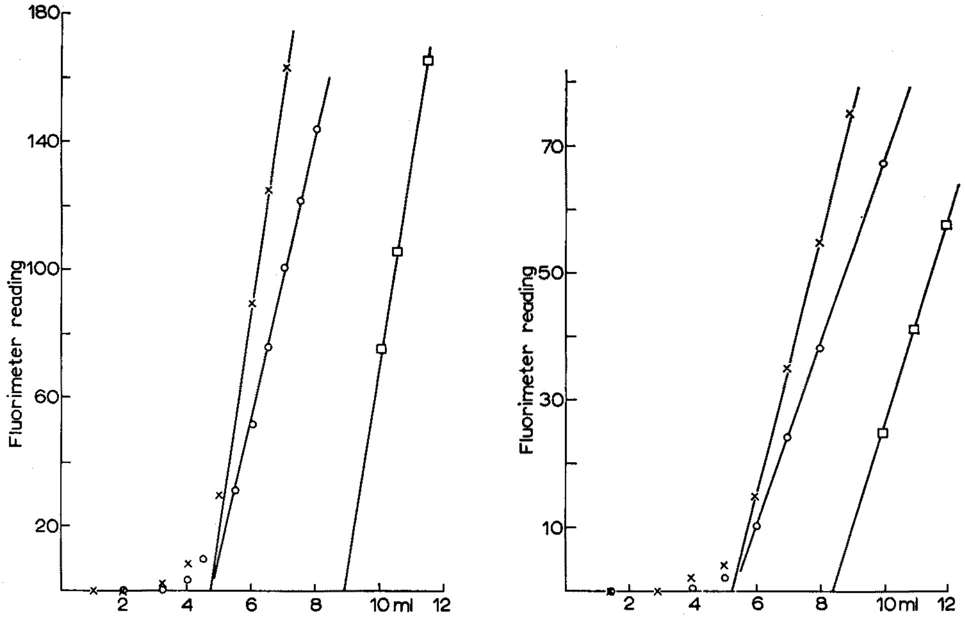
EFFECT OF ORDER OF ADDITION OF CATIONS

(Fluorescence measured 5 min after addition of second cation)

Flask no.	*10^{-3} M Pd(II) (ml)*	*10^{-3} M $OxSO_3^{2-}$ (ml)*	*10^{-3} M Mg(II) (ml)*	*Fluor.*
1	1.00	1.00	0	0
2	0	1.00	1.00	20
3	1.00	1.00	1.00[a]	2
4	1.00	1.00	1.00[b]	0
5	1.00[b]	1.00	1.00	19

[a] Cation added 5 min after the other cation.
[b] Cation added 15 min after the other cation.

Since most bivalent transition metal cations react rapidly with the fluorescent magnesium(II), cadmium(II) and/or zinc(II) complexes, it is possible that this reaction might be due to a rapid reaction of the cation with dissociated ligand, followed by rapid dissociation of the labile complex to give more free ligand. The slow reaction with palladium(II) would then be explained by a slow formation of the palladium(II) complex with the free ligand. The data of Table I were collected to test this possibility, using solutions of palladium(II), magnesium(II) and the ligand (designated $OxSO_3^{2-}$ in the Table), at a pH of 7. In these tests, the substance added



Figs. 1–2. Titration of Cu(II) and Pd(II) with (1) ZnL_2^{2-}, (2) CdL_2^{2-} complexes at pH 7. (×) $5\cdot10^{-3}$ mmole of Cu(II); (○) (□) $5\cdot10^{-3}$ mmole of Cu(II) + $4\cdot10^{-3}$ mmole Pd(II), (○) before heating, (□) after heating and further titration.

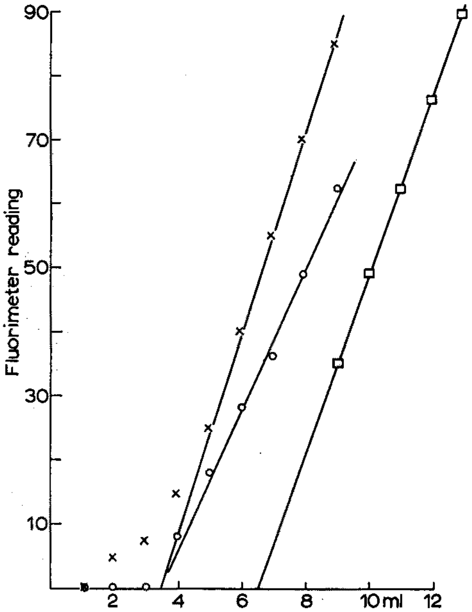


Fig. 3. Titration of Ni(II) and Pd(II) with CdL_2^{2-} complexes at pH 7. (×) $3.2\cdot10^{-3}$ mmole of Ni(II); (○) (□) $3.2\cdot10^{-3}$ mmole of Ni(II) + $3\cdot10^{-3}$ mmole Pd(II), (○) before heating, (□) after heating and further titration.

last was transferred after the solution had been made up to almost 100 ml in a volumetric flask. It was found that the order of addition made a difference when the cations were put into a solution containing sufficient ligand to complex only one of the cations. From Table I it can be seen that the palladium(II) reaction with the free ligand is not a slow one.

Figure 4 shows the rate at which palladium(II) replaces zinc(II) in its fluorescent complex to form a non-fluorescing complex. The data shown in Fig. 4 are for the case in which the concentration of palladium(II) ion was equivalent to that of the ZnL_2^{2-} complex. Other mixtures in which one or the other was in excess gave similar graphs. A comparison of this graph with the data of Table I, and consideration of the fact that copper(II), nickel(II) and cobalt(II) all react rapidly with the zinc complex, make it probable that the reactions take place through the formation of an intermediate addition complex,

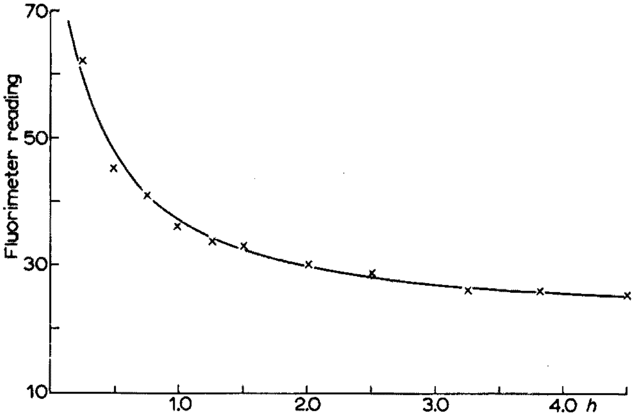


Fig. 4. The rate of reaction between Pd(II) and the ZnL_2^{2-} complex.

$$M^{2+} + ZnL_2^{2-} \rightleftharpoons MZnL_2 \rightleftharpoons ML_2^{2-} + Zn^{2+} \qquad (1)$$

It may be considered that all of the bivalent cations reacting will form an intermediate according to reaction (1), the difference between palladium(II) and the others being due to the way in which the complex–cation intermediate decomposes. In explaining results obtained with other complexes of the bivalent cations, CHABEREK AND MARTELL[3] have stated that bivalent cations form sp^3 hybrids, with the exception of palladium(II), which forms dsp^2 hybrids. If this assumption is made for the complexes considered in this paper, the slow reaction of palladium(II) can be explained by the necessity for bond rearrangement before the reaction can release PdL_2^{2-} and Zn^{2+}.

When M^{2+} in reaction (1) is any bivalent cation other than palladium(II), it may be assumed that the cation replacing the zinc(II) (or magnesium(II) or cadmium(II)) in the complex simply moves into the 8-electron ring formed by the two ring nitrogen atoms and the two hydroxyl oxygens, as the zinc(II) moves away, in a sort of *cis–trans* replacement.

Since the titration results indicate that the palladium(II) complex should be more stable than the ZnL_2^{2-} complex (the most stable of the fluorescent complexes of bivalent cations), it was decided to attempt to determine the overall formation constant of PdL_2^{2-} by fluorescent methods. Mixtures of the palladium(II) solution and the ZnL_2^{2-} complex were prepared and brought to equilibrium. In Fig. 5, it can be seen that there is a definite small fluorescence at the end-point of the titration (5.85 ml). In order to compare this fluorescence with that of the same amount of ZnL_2^{2-}, two solutions were prepared containing 5.00 and 6.00 ml of the ZnL_2^{2-} complex with no palladium(II) present. From these values, the fluorescence to be expected for a solution containing 5.85 ml was calculated, to check the fluorescence value produced by using 5.85 ml of ZnL_2^{2-} solution. Since calculations from the known constants for ZnL_2^{2-} show that it is over 99.9% in the form of ZnL_2^{2-} at a pH of 7, it may be assumed that the more stable PdL_2^{2-} complex will also be at least 99.9% in this form also. In this case the overall reaction may be assumed to be

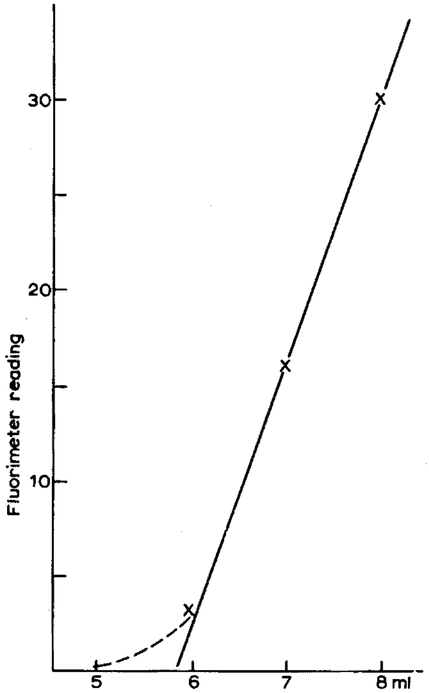


Fig. 5. Titration of Pd(II) with the ZnL_2^{2-} complex after heating.

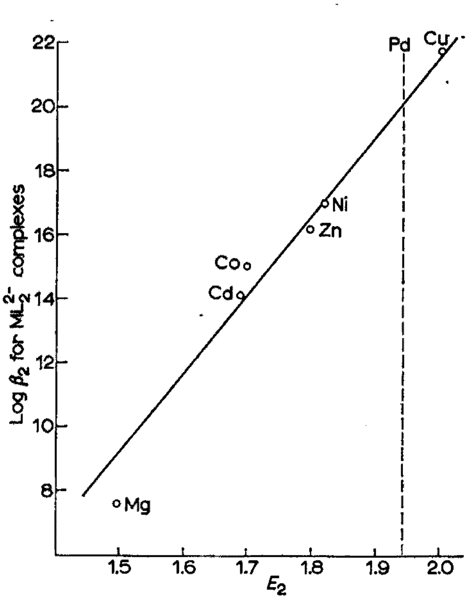


Fig. 6. Correlation of stabilities of ML_2^{2-} complexes with the second ionization potential of the cation involved.

$$ZnL_2^{2-} + Pd^{2+} \rightleftharpoons PdL_2^{2-} + Zn^{2+} \tag{2}$$

At the equivalence point, $PdL_2^{2-} = Zn^{2+}$ and $Pd^{2+} = ZnL_2^{2-}$, hence

$$K_{eq} = \frac{[PdL_2^{2-}]\,[Zn^{2+}]}{[Pd^{2+}]\,[ZnL_2^{2-}]} = \frac{\beta_{2PdL_2}}{\beta_{2ZnL_2}} \tag{3}$$

At equilibrium, if the fluorescence of the mixture $= f$, and the fluorescence of ZnL_2 $= F$, then the fraction of ZnL_2^{2-} and of Pd^{2+} is f/F, and the fraction of Zn^{2+} and of

PdL_2^{2-} is $(F-f)/F$. If these values are substituted in eqn. (3), then

$$K_{eq} = f^2/(F-f)^2 \tag{4}$$

and

$$\log K_{eq} + \log \beta_{2ZnL_2} = \log \beta_{2PdL_2} \tag{5}$$

When the experimentally determined fluorescence values are substituted in eqn. (5), it is found that

$$\log \beta_{2PdL_2} = 20.4$$

In order to have an independent check on this value, the logarithms of overall formation constants[2] were plotted against the second ionization constants of the metals involved[4]. This type of plot has been made for other complexes[3]. The results are shown in Fig. 6. When the second ionization potential for palladium is used in conjunction with this graph, the value for log β_2 for the complex between palladium(II) and the anion of 8-quinolinol-5-sulfonic acid is approximately 20, which is in good agreement with the result by fluorescence.

SUMMARY

Anomalous results for the reaction between palladium(II) and fluorescent complexes of 8-quinolinol-5-sulfonic acid were found to be due to a slow reaction. Heating the solution permits the determination of palladium(II) in combination with copper(II) or nickel(II), the two cations being titrated stepwise. The approximate value for the overall formation constant of the PdL_2^{2-} complex was determined.

RÉSUMÉ

Les anomalies trouvées dans les résultats obtenus par la réaction entre palladium(II) et acide 8-quinolinol-5-sulfonique semblent être dues à la lenteur de la réaction. Le chauffage de la solution permet le dosage du palladium en présence de cuivre ou de nickel. La valeur approximative de la constante de formation du complexe PdL_2^{2-} est donnée.

ZUSAMMENFASSUNG

Es konnte gezeigt werden, dass anomale Ergebnisse bei der Reaktion zwischen Palladium(II) und den fluoreszierenden Komplexen von 8-Chinolin-5-sulfonsäure auf eine langsame Reaktion zurückzuführen sind. Durch Erhitzen der Lösung ist es möglich, Palladium(II) zusammen mit Kupfer(II) oder Nickel(II) zu bestimmen, da die Kationen schrittweise titriert werden können. Ein Näherungswert für die Gesamtbildungskonstante des PdL_2^{2-}-Komplexes wurde bestimmt.

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DIE QUANTITATIVE BESTIMMUNG VON ALKALI- UND ERDALKALIIONEN DURCH FÄLLUNGSTITRATION IN NICHTWÄSSRIGEN LÖSUNGEN

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(Eingegangen den 4. März, 1967)

In einer früheren Mitteilung[1] hatten wir gezeigt, dass die im Vergleich zu Wasser oft völlig veränderten Löslichkeitsverhältnisse vieler Salze in nichtwässrigen Medien sich zu quantitativen Fällungsreaktionen ausnutzen lassen, die in wässriger Lösung nicht denkbar sind. So konnten in verschiedenen Ketonen und Azetonitril die dort gut löslichen Jodide der Alkalimetalle mit einer Lithiumchlorid enthaltenden alkoholischen oder ketonischen Masslösung titriert werden, wobei sich der Fehler innerhalb der Grenzen ±1% bewegte und die Standardabweichung zu 0.6% bestimmt wurde.

Zum Zwecke des späteren Vergleichs zeigt Fig. 1 die mit oszillometrischer Indikation** in den verwendeten Lösungsmitteln für die Fällungsreaktion

$$\mathrm{Me^+ + J^- + Li^+ + Cl^- = MeCl\downarrow + Li^+ + J^-}$$

erhaltenen charakteristischen Kurventypen.

Es war bereits angekündigt worden, dass die Untersuchungen auf in diesen Medien lösliche Alkalisalze mit anderen Anionen als Jodid und auf Erdalkalisalze erweitert werden sollten. Bezüglich experimenteller Einzelheiten sei auf[1] verwiesen.

ERGEBNISSE

Die Titration von Natriumperchlorat und von Kaliumhexafluoroarsenat

Natriumperchlorat wurde in einer Vorlage von 100 ml Azeton mit einer 0.2060 *N* Masslösung von Lithiumchlorid in Azeton titriert. Dabei fiel, wie bei der Titration von Natriumjodid, schwerlösliches Natriumchlorid aus. Im Gegensatz zu den Ergebnissen bei der Titration der Alkalijodide lieferte die oszillometrische Messung des Umsetzungsgrades in Abhängigkeit von der Reagenzzugabe hier jedoch nur sehr stumpfe, schlecht auswertbare Schnittwinkel, wie die Diagramme I und II auf Fig. 2 für zwei Beispiele mit den dort angegebenen Probenmengen zeigen. Die gestrichelten Vertikalen sollen jeweils den errechneten theoretischen Äquivalenzpunkt kennzeichnen.

Auch die unter analogen Bedingungen ausgeführte Titration von Kaliumhexafluoroarsenat war wenig erfolgreich. Es trat überhaupt kein auswertbarer Knick

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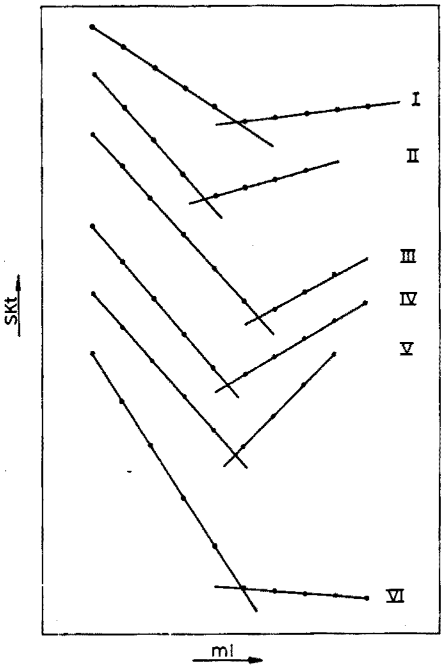
** System E. PUNGOR, hergestellt von RADELKIS, Budapest.

auf (III, Fig. 2) oder ebenfalls ein Schnittwinkel nahe 180° (IV, Fig. 2). Doch wurde dabei nicht wie bisher die charakteristische V-Form der Kurvenzüge gefunden, sondern ihre Umkehrung. Der Ersatz von Kaliumionen durch Lithiumionen bei der Ausfällung von Kaliumchlorid durch das Reagenz Lithiumchlorid führte hier also nicht zu einer Abnahme des Leitwertes, wie früher[1] bei der Titration von Kaliumjodid beobachtet worden und nach Lage der Ionenbeweglichkeiten auch zu erwarten war.



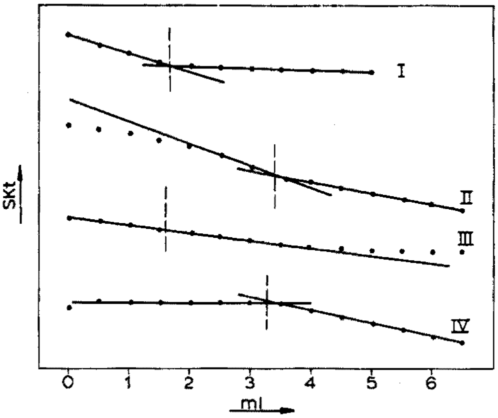


Fig. 1. Oszillometrisch indizierte Titrationen von Natriumjodid in verschiedenen Ketonen. (I) 1180 Val$\cdot 10^{-6}$ in Azeton; (II) 1400 Val$\cdot 10^{-6}$ in Butanon; (III) 1416 Val$\cdot 10^{-6}$ in Cyclohexanon; (IV) 1180 Val$\cdot 10^{-6}$ in Azetophenon; (V) 1180 Val$\cdot 10^{-6}$ in Methyl-isobutylketon; (VI) 1180 Val$\cdot 10^{-6}$ in Methyl-isobutylketon. Titriert mit LiCl in Äthanol 0.2550 N (I, III, IV, V), LiCl in Äthanol 0.3750 N (II) und mit LiCl in Methyl-isobutylketon 0.2575 N (VI).

Fig. 2. Oszillometrisch indizierte Titration in Azeton mit LiCl in Azeton 0.2060 N. (I) 349 Val$\cdot 10^{-6}$ $NaClO_4$; (II) 698 Val$\cdot 10^{-6}$ $NaClO_4$; (III) 340 Val$\cdot 10^{-6}$ $KAsF_6$; (IV) 680 Val$\cdot 10^{-6}$ $KAsF_6$.

Wir versuchten anschliessend die Titration von Natriumperchlorat in einer Vorlage von 100 ml Methyl-isobutylketon und mit einer Masslösung von Lithiumchlorid in Methyl-isobutylketon (ebenfalls 0.2060 N). Dabei wurden in jedem Falle in schroffem Gegensatz zu den Resultaten bei der Titration der Alkalijodide in den Ketonen (auch Methyl-isobutylketon, vgl. Fig. 1) und denen der Titration des Natriumperchlorats in Azeton (vgl. Fig. 2) bis zum Äquivalenzpunkt steil ansteigendeKurvenäste (Leitwerte) erhalten, wie auf Fig. 3 an einigen Beispielen gezeigt wird. Hier liessen sich die Ergebnisse im wesentlichen ebenfalls innerhalb einer Fehlergrenze von ±1% auswerten. Lediglich bei sehr kleinem Reagenzverbrauch (I, Fig. 3) traten etwas grössere Abweichungen auf.

Auch die Titration von Kaliumhexafluoroarsenat war in Methyl-isobutyl-

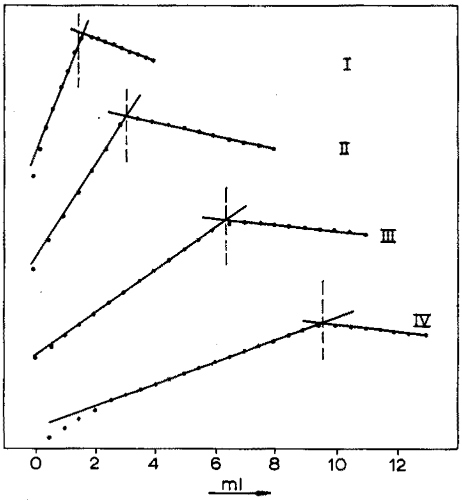


Fig. 3. Oszillometrisch indizierte Titration von $NaClO_4$ in Methyl-isobutylketon mit LiCl in Methyl-isobutylketon 0.2060 *N*. (I) 330 Val·10^{-6}; (II) 660 Val·10^{-6}; (III) 1320 Val·10^{-6}; (IV) 1980 Val·10^{-6}.

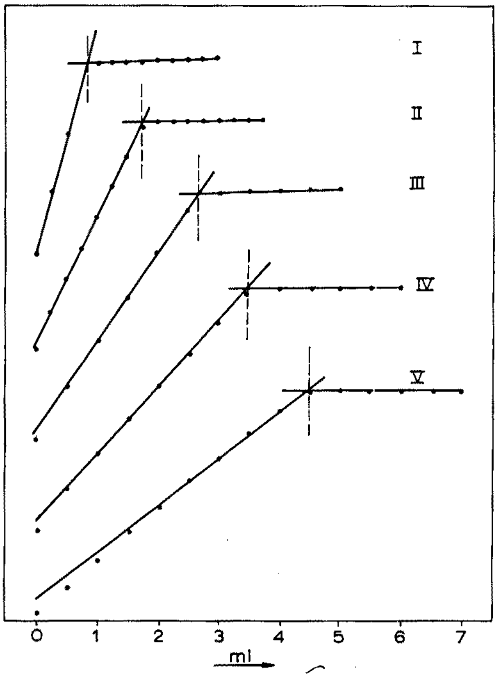


Fig. 4. Oszillometrisch indizierte Titration von $KAsF_6$ in Methyl-isobutylketon mit LiCl in Äthanol 0.2550 *N*. (I) 230 Val·10^{-6}; (II) 460 Val·10^{-6}; (III) 690 Val·10^{-6}; (IV) 920 Val·10^{-6}; (V) 1150 Val·10^{-6}.

keton gut durchführbar. Die Zunahme des Leitwertes bis zum Äquivalenzpunkt war dabei noch erheblich grösser als beim Natriumperchlorat, was sich in einem noch steileren Anstieg als dort äusserte. Figur 4 zeigt oszillometrisch bestimmte Diagramme, wie sie bei Titrationsserien von Kaliumhexafluoroarsenat in Methyl-isobutylketon mit Lithiumchlorid in Äthanol als Masslösung (0.2550 *N*) erhalten wurden. Sieht man auch hier von den Konzentrationsextremen (I und V, Fig. 4) ab, dann liegen die Maximalfehler ebenfalls regelmässig unterhalb der Grenzen von ±1%. Die Titration von Kaliumhexafluoroarsenat in Methyl-isobutylketon wurde ausserdem mit einer Masslösung von Lithiumchlorid in Methyl-isobutylketon ausgeführt. Dabei erhielten wir ganz analoge Ergebnisse. Lediglich bei den grösseren Konzentrationen traten kurz vor dem Äquivalenzpunkt Abweichungen vom linearen Anstieg auf, die eine quantitative Auswertung erschweren bzw. unsicher machen.

Zum Vergleich wurden die beschriebenen Reaktionen auch konduktometrisch* indiziert. Figur 5 zeigt hierfür drei Beispiele:

(I) Die Titration von Natriumjodid in Methyl-isobutylketon mit Lithiumchlorid in Metyl-isobutylketon. Das Diagramm entspricht dem oszillometrisch gemessenen Kurvenzug VI auf Fig. 1.

(II) Die Titration von Natriumperchlorat in Methyl-isobutylketon mit

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* Conductivity Meter, hergestellt von RADELKIS, Budapest.

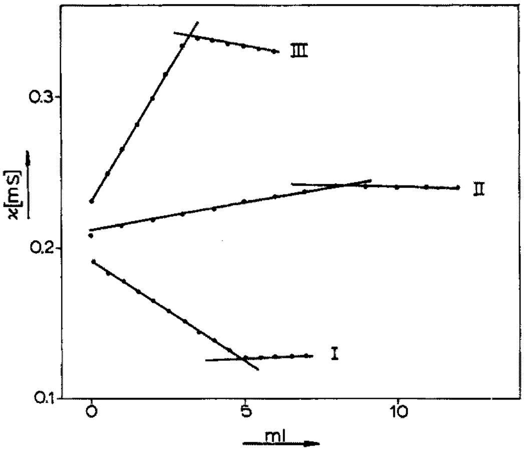


Fig. 5. Konduktometrisch indizierte Titration in Methyl-isobutylketon mit LiCl in Methyl-isobutylketon. (I) 1180 Val·10^{-6} NaJ mit LiCl 0.2575 N; (II) 1300 Val·10^{-6} $NaClO_4$ mit LiCl 0.2060 N; (III) 680 Val·10^{-6} $KAsF_6$ mit LiCl 0.2060 N.

Lithiumchlorid in Methyl-isobutylketon, entsprechend dem oszillometrisch gemessenen Kurvenzug III auf Fig. 3.

(III) Die Titration von Kaliumhexafluoroarsenat in Methyl-isobutylketon, ähnlich dem oszillometrischen Diagramm IV auf Fig. 4.

Die konduktometrische Anzeige bestätigt in allen Fällen die Ergebnisse der oszillometrischen Messungen: Bei der Titration der Alkalijodide tritt in allen verwendeten Ketonen bis zum Äquivalenzpunkt der Reaktion eine mehr oder minder starke Abnahme der Leitfähigkeit auf. Bei der Titration von Natriumperchlorat in Methyl-isobutylketon dagegen steigt die Leitfähigkeit. In noch weit stärkerem Masse ist das bei der Titration des Kaliumhexafluoroarsenats der Fall.

Die Titration von Bariumperchlorat

1310 Val·10^{-6} Bariumperchlorat wurden einmal in einer Vorlage von 100 ml Methyl-isobutylketon, das andere Mal in einer Vorlage von 100 ml Azeton mit einer Lösung von Lithiumchlorid in Methyl-isobutylketon titriert. In beiden Fällen wurden prinzipiell richtige Ergebnisse gefunden, doch waren die oszillometrisch erhaltenen Diagramme bis zum Äquivalenzpunkt der Reaktion etwas gekrümmt. Das erschwert natürlich die Ermittlung des Äquivalenzpunktes und macht sie ungenau. Deshalb wurde versucht, durch Variation der Versuchsbedingungen Möglichkeiten zu finden, die diese Krümmungen zu vermeiden gestatten. Die Titration des Bariumperchlorats in einer Vorlage von 100 ml Methyl-isobutylketon zeigte, dass bei Verringerung der Konzentration des Bariumperchlorats erst unterhalb 30 Val·10^{-6} lineare Anzeigen erhalten wurden. Dagegen wurde dieses Ziel bei Verwendung von Azeton als Lösungsmittel bereits unterhalb 100 Val·10^{-6} Bariumperchlorat erreicht.

Figur 6 zeigt, dass es unterhalb dieser Grenze möglich ist, aus einer Lösung von Bariumperchlorat Bariumchlorid zu fällen und den Äquivalenzpunkt oszillometrisch zu indizieren. Die Titrationsdiagramme ähneln im Typ dabei den bei den Alkaliperchloraten (vgl. Fig. 3) erhaltenen, nur muss die Konzentration des Barium-

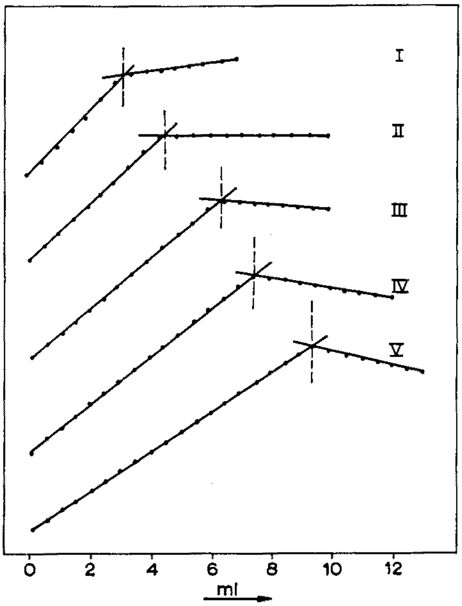


Fig. 6. Oszillometrisch indizierte Titration von $Ba(ClO_4)_2$ in Azeton mit LiCl in Methyl-isobutylketon 0.00825 *N*. (I) 26.25 $Val \cdot 10^{-6}$; (II) 36.7 $Val \cdot 10^{-6}$; (III) 52.5 $Val \cdot 10^{-6}$; (IV) 63.0 $Val \cdot 10^{-6}$; (V) 78.75 $Val \cdot 10^{-6}$.

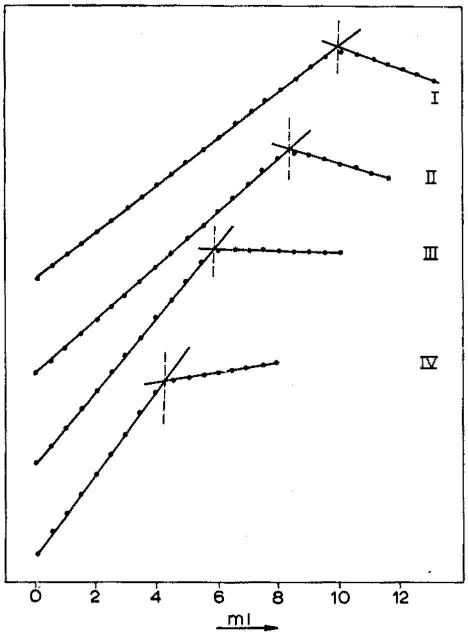


Fig. 7. Oszillometrisch indizierte Titration von BaJ_2 in Azeton mit LiCl in Methyl-isobutylketon 0.00825 *N*. (I) 81.0 $Val \cdot 10^{-6}$; (II) 67.5 $Val \cdot 10^{-6}$; (III) 47.2 $Val \cdot 10^{-6}$; (IV) 33.7 $Val \cdot 10^{-6}$.

perchlorats eine Zehnerpotenz niedriger liegen als dort, um lineare oszillometrische Anzeige zu gewährleisten.

Die Titration von Bariumjodid

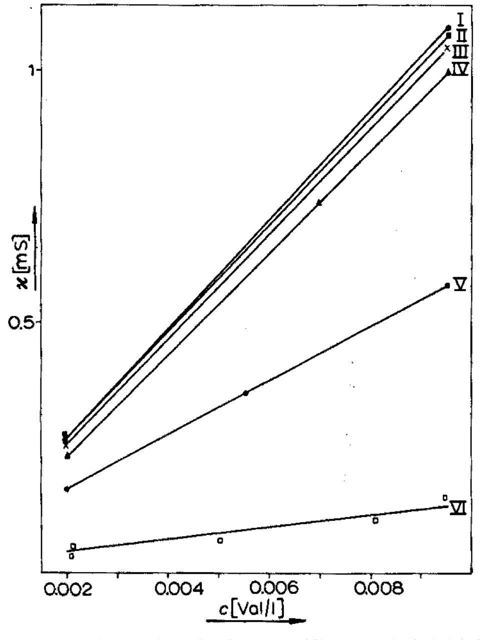
Auch hier lässt sich bei geeigneter Verdünnung die Fällungstitration oszillometrisch linear indizieren. Bei Verwendung von 100 ml Azeton als Lösungsmittelvorlage wird dieser Bereich bereits unterhalb 200 $Val \cdot 10^{-6}$ erreicht. Das sei an einigen Beispielen auf Fig. 7 veranschaulicht. Sie zeigen die Bestimmung des Bariums in einer Lösung von Bariumjodid in Azeton. Entsprechend den geringen Konzentrationen des Bariums musste hier, wie übrigens auch schon bei den Beispielen von Fig. 6 mit einer stark verdünnten Masslösung von Lithiumchlorid (0.00825 *N*) gearbeitet werden, damit der Verbrauch gross genug und der Ablesefehler klein blieb.

Lösungen von Bariumjodid in den Ketonen besitzen gegenüber denen von Bariumperchlorat den Nachteil, dass sie durch Einwirkung von Licht und Luft langsam unter Abscheidung von Karbonat und Verfärbung durch Jod ihren Titer verändern. Deshalb wird im allgemeinen bei den Erdalkalien den Lösungen der Perchlorate der Vorzug zu geben sein.

DISKUSSION

Oszillometrische und konduktometrische Indikation der untersuchten Fällungstitrationen zeigen: Die Ausfällung der Alkalien aus den Lösungen der Jodide ist in allen als Lösungsmittel verwendeten Ketonen regelmässig mit einer Abnahme der Leitfähigkeit der Lösungen verbunden. Bei der analogen Fällung des Natriums aus der Lösung des Perchlorats in Azeton ist kaum eine Leitfähigkeitsänderung zu beobachten. Das Gleiche gilt, wenn aus einer azetonischen Lösung von Kaliumhexafluoroarsenat Kalium gefällt wird. Dagegen gibt die Titration von Natriumperchlorat oder Kaliumhexafluoroarsenat in einer Lösung von Methyl-isobutylketon eine starke Zunahme der Leitfähigkeit. Schliesslich wird bei der Titration von Bariumjodid oder Bariumperchlorat in allen verwendeten Ketonen eine sehr starke Zunahme der Leitfähigkeit gefunden.

Das zeigt eindeutig, dass sich der Verlauf der Titrationsdiagramme in den verwendeten nichtwässrigen Lösungsmitteln im allgemeinen nicht aus den entsprechenden Ionenbeweglichkeiten vorhersagen lässt, wie das bei Wasser als Lösungsmittel möglich ist. Die Ursache hierfür ist die unvollständige Dissoziation der Salze in den Ketonen. Die Leitfähigkeit dieser Lösungen wird in weit stärkerem Masse von dem Dissoziationsgrad des betreffenden Salzes in dem betreffenden Lösungsmittel bestimmt, als von den Beweglichkeiten der beteiligten Ionen.



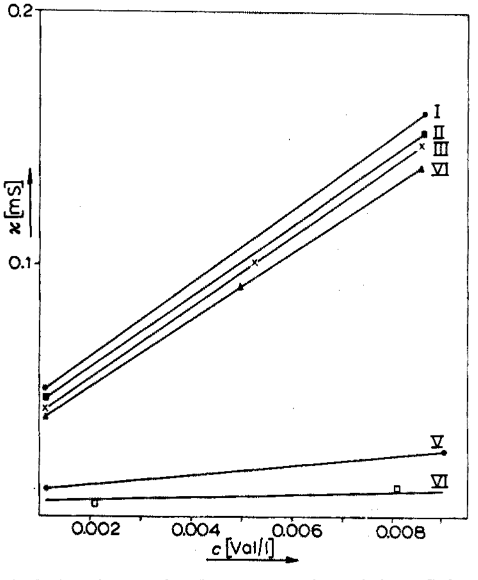


Fig. 8. Abhängigkeit der spezifischen Leitfähigkeit bei 25° von der Konzentration einiger Salze in Azetonlösung. (I) $LiClO_4$; (II) $NaClO_4$; (III) NaJ; (IV) LiJ; (V) $Ba(ClO_4)_2$; (VI) LiCl.

Fig. 9. Abhängigkeit der spezifischen Leitfähigkeit bei 25° von der Konzentration einiger Salze in Methyl-isobutylketon-Lösung. (I) $LiClO_4$; (II) $NaClO_4$; (III) NaJ; (IV) LiJ; (V) $Ba(ClO_4)_2$; (VI) LiCl.

Zur Deutung der Ergebnisse muss deshalb die Leitfähigkeit der zu titrierenden Salze mit der Leitfähigkeit der bei der Titration entstehenden Salze in den angewandten Lösungsmitteln und bei den vorliegenden Konzentrationen verglichen werden. Wir zeigen das an Hand einiger Beispiele für Azeton (Fig. 8) und Methyl-isobutylketon (Fig. 9). Die Leitfähigkeitswerte zur Konstruktion dieser Diagramme sind teils aus der Literatur[2] entnommen, teils entstammen sie eigenen Messungen, die später dargestellt werden sollen.

Die äusserst geringen Leitfähigkeitsdifferenzen zwischen Natriumperchlorat in Azeton (II, Fig. 8) und Lithiumperchlorat in Azeton (I, Fig. 8) im Konzentrationsbereich unserer Titrationen zeigen z.B., dass hier keine markanten Leitfähigkeitsänderungen zu erwarten sind, was mit unseren Titrationsdiagrammen (I und II, Fig. 2) übereinstimmt. Dagegen ist der Unterschied zwischen Natriumjodid und Lithiumjodid (III und IV, Fig. 8) grösser und ermöglicht eine Indizierung des Äquivalenzpunktes (s.a. I, Fig. 1). Besonders starke Leitfähigkeitszunahmen sind bei der Titration von Bariumperchlorat zu erwarten, wie durch Vergleich der Kurvenzüge I und V (Fig. 8) deutlich wird, und von uns auch gefunden wurde.

Bei Verwendung von Methyl-isobutylketon als Lösungsmittel tritt eine stärkere Differenzierung der Leitfähigkeiten (Fig. 9) in dem betrachteten Konzentrationsbereich auf. Dadurch wird auch die Titration von Natriumperchlorat möglich. Hier erfolgt in Übereinstimmung mit unseren Ergebnissen (Fig. 3) eine Zunahme der Leitfähigkeit bis zum Äquivalenzpunkt, wie durch Vergleich der Kurvenzüge I und II auf Fig. 9 vorherzusehen ist. Vergleich von III und IV (Fig. 9) zeigt, dass auch in Methyl-isobutylketon die Leitfähigkeit abnimmt, wenn man Natriumjodid titriert. Der Vergleich von I und V (Fig. 9) schliesslich zeigt, dass eine äusserst starke Zunahme der Leitfähigkeit zu erwarten ist, wenn man Bariumperchlorat titriert. Das zeigen auch unsere Titrationsdiagramme (Fig. 6). Sie wurden im Falle der Bariumsalze nur mit einem Viertel der Maximalempfindlichkeit des Oszillotitrators aufgenommen. Wenn auch die Absolutwerte der Leitfähigkeitsänderungen in Methyl-isobutylketon kleiner sind als in Azeton, wirkt sich dieser Nachteil nur bei der konduktometrischen Indikation der Titrationen aus. Bei der oszillometrischen Indikation wird er durch die zunehmende Empfindlichkeit des Gerätes bei der geringeren DK kompensiert.

Anschliessend soll versucht werden, die Bedingungen und Grenzen für eine Titration der Alkalien und Erdalkalien nebeneinander zu ermitteln.

ZUSAMMENFASSUNG

Die quantitative Fällungstitration der Kationen der Salze Natriumperchlorat, Kaliumhexafluoroarsenat, Bariumperchlorat und Bariumjodid in Azeton und in Methyl-isobutylketon wurde untersucht. Als Massreagenz diente eine Lösung von Lithiumchlorid in den verwendeten Ketonen. Der Endpunkt wurde oszillometrisch und konduktometrisch indiziert. Die dabei erhaltenen verschiedenartigen Kurventypen konnten durch Vergleich der spezifischen Leitfähigkeiten der vorliegenden Salzlösungen mit denen der bei der Titration entstehenden gedeutet werden. Innerhalb einer Fehlergrenze von ±1% ist die Bestimmung von Bariumperchlorat und von Bariumjodid in beiden Ketonen möglich. Für Natriumperchlorat und Kaliumhexafluoroarsenat ist das nur in Methyl-isobutylketon, nicht aber in Azeton, der Fall.

SUMMARY

Precipitation titrations of the cations of salts such as sodium perchlorate, potassium hexafluoroarsenate, barium perchlorate and barium iodide, were investigated in acetone and methyl isobutyl ketone media. The titrant was a solution of lithium chloride in the same ketone and end-points were detected oscillometrically or conductometrically. The different types of titration curve found can be explained by comparing the specific conductivities of the solutions before and after titration. Barium iodide and barium perchlorate can be determined in both ketones with an error of ±1%. In the case of sodium perchlorate and potassium hexafluoroarsenate, accurate titrations are possible only in methyl isobutyl ketone media.

RÉSUMÉ

Les titrages par précipitation de cations de sels tels que perchlorate de sodium, hexafluoarsénate de potassium, perchlorate de baryum et iodure de baryum ont été examinés en milieu acétone et méthylisobutylcétone. On utilise comme réactif titrant une solution de chlorure de lithium dans la même cétone; les points finals sont détectés par oscillométrie ou par conductométrie. Les différents types de courbe de titrage trouvés peuvent s'expliquer en comparant les conductivités spécifiques des solutions avant et après titrage. L'iodure et le perchlorate de baryum peuvent être dosés dans les 2 cétones avec une erreur de ±1%. Dans le cas du perchlorate de sodium et de l'hexafluoarséniate de potassium, des titrages précis ne sont possibles qu'en milieu méthylisobutylcétone.

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A COMPARISON OF ELECTROMETRIC AND GASOMETRIC METHODS FOR FOLLOWING AUTOXIDATIONS*

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The commercial development of a reproducible electrode system for the convenient estimation of oxygen concentration in solution[1], has spurred its application in many systems. This electrode system has been used, for instance, in studies of the photophosphorylation of isolated chloroplasts[2,3], of mitochondrial respiration[4-7] and of the respiration of human leucocytes[8]. The oxygen electrode requires the use of a well-defined stable activating voltage, and the current produced (proportional to the oxygen concentration) is usually converted to a potential difference which can be recorded. In this report the application of the system in following the photosensitized autoxidation of an amino acid, histidine, is described and compared with the gasometric (Warburg) method for following the same reaction. Although such an application is not of unusual significance, the comparison of the two methods serves to emphasize some precautions which are necessary in the routine use of the electrode for the determination of oxygen concentrations. These precautions, although they are obvious on physico-chemical grounds[9,10], are seldom cited by those who use this system routinely; failure to apply them may lead to unwittingly large errors. It has previously been pointed out that the usual manometric techniques may underestimate oxygen consumption[11]. The results below will show that even in the absence of such evolution discrepancies in the kinetic rates evaluated by the two methods can result.

EXPERIMENTAL

Oxygen electrode

The "Clark oxygen electrode" (Yellow Springs Instrument Company, Yellow Springs, Ohio) was used. The polarizing voltage used for operation was 0.8 V supplied by a mercury battery. The current from the cell flowed through a 12,500-ohm sampling resistor and the resulting *i–R* drop was amplified using an operational amplifier. The amplified signal was recorded on a potentiometric recorder, with 0.5-sec response-time and 0.2% accuracy.

Gasometric apparatus

The automatic Warburg apparatus used was the Mechrolab model 401 "automanometer". In this apparatus the change in volume necessary to maintain a system

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at constant temperature at a constant pressure is translated into a voltage, which was recorded on the same recorder used above. This instrument was calibrated as recommended by the manufacturer, using air-saturated solutions, and oxygen solubilities from the International Critical Tables.

A mixture of 5.2% oxygen in nitrogen, analysed by the manufacturer to establish the exact oxygen content, 100% oxygen and pre-purified nitrogen were used for calibration of the oxygen electrode.

Buffer solutions were prepared from reagent-grade salts and the pH determined with a Beckman Zeromatic pH meter and a combination electrode. Dyes were purchased from Fisher, and were used without further purification. Polymethacrylic acid (PMA) (Borden Chemical Company), a high-molecular-weight polymer (molecular weight not specified), was dialyzed to remove low-molecular-weight fractions, and the residue freeze-dried. Polyvinyl pyrrolidone (PVP), molecular weight $3.6 \cdot 10^5$, was purchased from Antara Chemical Company.

For use, solutions in a simple rectangular vessel, closed to the atmosphere, and thermostatted at $25 \pm 0.1°$, were equilibrated with the gas mixture by bubbling the gas through the solution for 30 min before and during measurement. In order to remove oxygen from solutions, pre-purified nitrogen was passed through a chromium(II) chloride train before bubbling through the solution. Proper adjustment of the rate of magnetic stirring of the solutions was found to be extremely important in ensuring reproducibility of the measurements in both electrometric and gasometric procedures. Illumination was carried out by shining the light of a 500-W tungsten projector lamp through interference filters onto the transparent sidewall of the thermostat vessel.

The chemical determination of oxygen was made by the Standard Winkler Method[12], which is accurate to ±1%[13].

RESULTS

The signal recorded from the oxygen electrode in water equilibrated with air was 31.5 mV when the current flowed through a 12.5-ohm resistor; the current output was therefore 2.56 μA.

The oxygen electrode was calibrated by equilibrating appropriate aqueous solutions with gas mixtures containing oxygen at known partial pressures. These solutions were then analyzed chemically for dissolved oxygen[12], and in identical solutions the reading developed by the electrode was measured on the recorder (as well as on a Keithly model 660 differential voltmeter). The resulting data are shown in Fig. 1. In agreement with data (39% decrease) listed in the International Critical Tables[14], the solubility of oxygen in 2 M sodium chloride was found to be decreased by 45% as compared with that in water. The 13.5% decrease in solubility observed for buffered solutions at 0.05 ionic strength did not vary over the wide pH range used; the addition of the (uncharged) polymer PVP caused a 23% decrease, whereas the addition of a comparable amount of PMA (an anionic polymer at neutral pH) caused a 71.5% decrease in oxygen solubility. It is apparent that although the chemical potential of oxygen (and therefore the current developed at the electrode) in the various air-saturated solutions is identical, the actual concentration of oxygen is not the same. From the data in Fig. 1 it can be calculated that if an electrode were calibrated in pure water and then used to determine the change in oxygen concentration in a reaction occurring in pH 7 buffer, the error engendered would be 13.5%.

As might be expected, the polarographic technique is more sensitive than the gasometric one for following changes in oxygen concentration during a reaction. This was demonstrated by following the rate of oxygen consumption in the course of the photo-oxidation of histidine, sensitized by rose bengal. The reaction mixture consisted of $2 \cdot 10^{-3}$ *M* histidine and $2 \cdot 10^{-5}$ *M* rose bengal dissolved in a phosphate–citrate buffer of pH 7.0, ionic strength 0.05. The mixture was equilibrated with air, and upon irradiation with light at 548 nm, the decrease in oxygen concentration was followed in the closed system both manometrically and with the oxygen electrode. The time course of the reaction as followed by the two methods is shown in Fig. 2. By following the reaction in the automanometer in the presence and absence of 1% boric acid or 10% potassium hydroxide[15], it was established that neither ammonia nor carbon

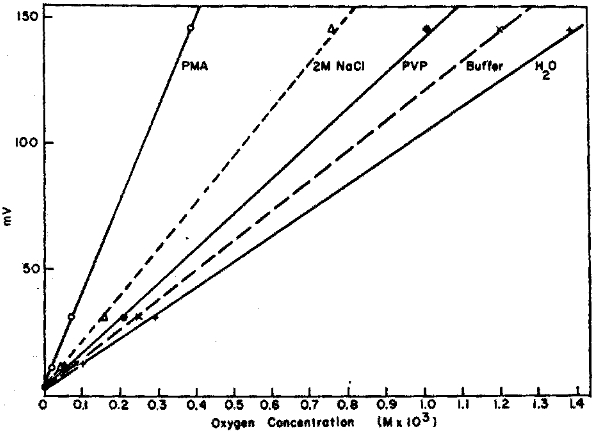

Fig. 1. Calibration of oxygen electrode in various solutions equilibrated with 5.2% O_2/N_2, air, 100% O_2 and de-oxygenated nitrogen. "Buffer" was pH 4.0 and 7.0 phosphate–citrate buffer, and pH 9.0 Tris buffer, all at ionic strength 0.05. "PMA" and "PVP" solutions consisted of 1% polymer in pH 7.0 buffer.

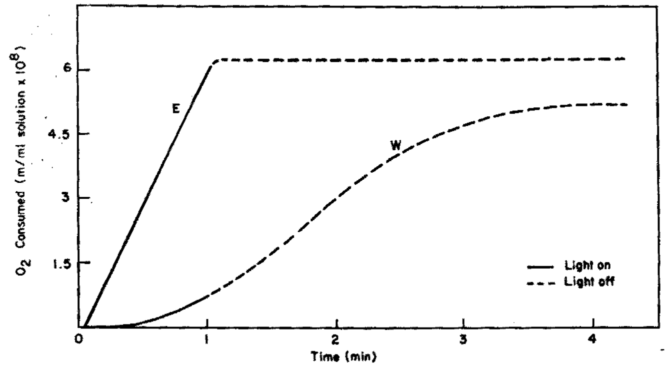

Fig. 2. Time course of sensitized photo-oxidation. $2 \cdot 10^{-3}M$ histidine, $2 \cdot 10^{-5}$ *M* rose bengal, pH 7.0 buffer; irradiated with light at 548 nm for 1 min. E, W= reaction followed with electrode or Warburg respectively.

dioxide was evolved. However, when the Warburg apparatus was used, there was an apparent induction period in the reaction. The manometric method primarily measured the decrease of oxygen in the gas phase, whereas the oxygen was being consumed in the solution phase. The time lag noted was presumably due to the time needed to re-establish the requisite equilibrium ratios of oxygen concentrations in the gas and aqueous phase. For this reason, the gasometric method, although inherently as sensitive as the electrometric one, was actually less sensitive to small changes occurring in the solution phase in short times. The need to re-establish new equilibrium conditions also accounted for the apparent post-illumination dark reaction in the case of the photo-oxidation followed by the gasometric method. When the reaction was followed with the oxygen electrode, the consumption of oxygen was seen to stop as soon as the light had been turned off. The total oxygen consumption of the photochemical reaction measured by the two different methods differed by 16.7%. This difference in oxygen consumption evaluated by the two methods varied from 1.8% to 25.3%, averaging 11.4%, when the reaction was carried out at different pH, and in the absence or presence of a soluble polymer to bind the sensitizer[16]. The reproducibility of measuring the rate of the reaction was ±9.8% for the Warburg method and ±6.13% for the oxygen electrode. These factors may thus account for the 11.4% difference noted above.

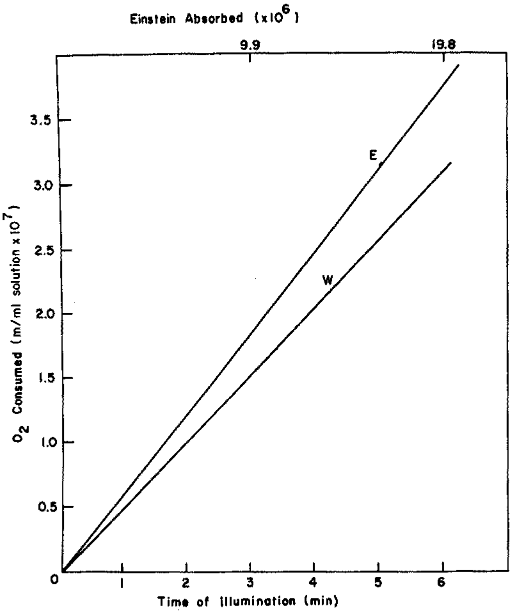

Fig. 3. Oxygen consumption of sensitized photo-oxidation as a function of time of illumination. Conditions as in Fig. 2.

Figure 3 illustrates the oxygen consumption determined in the photosensitized oxidation of histidine followed by both methods, as a function of time of illumination. It can be seen that the oxygen consumption increased linearly with the time of illumination, at least for the first 6 min of irradiation. There was thus no apparent "dark reaction" in this particular system.

DISCUSSION

The oxygen electrode is usually calibrated by equilibrating water with nitrogen, air or oxygen, the composition of the supporting (usually aqueous) solution rarely being considered or specified[2–5,11,17,18]. Only seldom is it noted[8–10] that calibration must take place in a solvent of the same ionic composition as that in which the subsequent routine measurements will be conducted. If solutions differing in chemical composition are equilibrated with oxygen at the same partial pressure, the actual concentrations of oxygen may differ, even though, after equilibration, the chemical potential of oxygen must be the same in all the media. In characterizing the change in the diffusion current of oxygen at the dropping mercury electrode in media of differing viscosity, JORDAN *et al.*[13] showed that the diffusion is determined by the activity rather than by the concentration gradient of the solution. The same considerations apply in solutions of different ions. From the data of Fig. 1 it can be seen that the electrode must be calibrated against known oxygen contents in solutions, the compositions of which are similar to those in which subsequent reactions will be carried out.

From Fig. 2 it is apparent that, although inherently the gasometric method is as sensitive as the electrometric one, the need to re-establish equilibrium concentrations of dissolved gas makes this method less sensitive to small changes, when these occur in relatively small periods of time. Contrary to what has often been stated[15], the slow rate of diffusion of the gas into the liquid phase limits the utility of gasometric devices in the kinetic elucidation of chemical reaction. When gas evolution accompanies the consumption of a second gaseous component, the gasometric method may often induce an apparent lag phase, which can be overcome by decreasing the reaction rate sufficiently[11]. In the rose bengal-sensitized photo-oxidation of histidine in which neither carbon dioxide nor ammonia evolution takes place, the time-lag in the gasometric determination appears because the reaction takes place too rapidly to allow for oxygen dissolution into the liquid phase. For many reactions, *e.g.* those in which it is desired to examine initial reaction rates free of possible complicating back- or side-reactions, the use of the oxygen electrode is therefore much to be preferred. The differences observed in oxygen consumption measured by the gasometric or polarographic procedure, have been noted by others[7,11,19]; the reproducibility of the two methods is comparable.

SUMMARY

Gasometric and electrometric methods for determining oxygen in the study of photosensitized reactions are compared. The oxygen electrode must be calibrated against known solutions similar in composition to the solutions used in the reactions that are studied. The electrode can be used to study initial reaction rates whereas this is impossible for fast reactions with the Warburg apparatus.

RÉSUMÉ

On a effectué une comparaison des méthodes gazométriques et électrométriques pour le dosage de l'oxygène dans l'étude des réactions photosensibilisées. L'électrode d'oxygène doit être calibrée à l'aide de solutions connues, de composition similaire aux solutions utilisées dans les réactions examinées. L'électrode peut être employée pour étudier les vitesses de réaction initiales, attendu que cela est impossible pour les réactions rapides, avec l'appareil de Warburg.

ZUSAMMENFASSUNG

Es wurden gasometrische und elektrometrische Methoden verglichen, die zur Bestimmung von Sauerstoff bei der Untersuchung photoempfindlicher Reaktionen dienen. Die Sauerstoffelektrode muss mit bekannten Lösungen geeicht werden, die ähnliche Zusammensetzungen besitzen wie die bei den Reaktionen verwendeten. Die Elektrode kann zur Untersuchung von Anfangsreaktionen verwendet werden. Dagegen ist es unmöglich, sie für schnelle Reaktionen mit der Warburg-Apparatur zu benutzen.

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LIQUID EXTRACTION OF MOLYBDOPHOSPHORIC AND MOLYBDOARSENIC ACIDS: APPLICATION TO THE DETERMINATION OF PHOSPHORUS IN THE PRESENCE OF ARSENIC

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(Received February 1st, 1967)

It is well known that heteropolyacids of the 12-acid type can be extracted from acidic aqueous solutions by some organic solvents. One of the earliest applications was the extraction of 12-molybdophosphoric acid into diethyl ether in order to isolate the acid to make a reagent for precipitating proteins[1]. SCROGGIE[2] found esters, ketones, aldehydes and ethers to be good extractants for 12-molybdophosphoric acid; KEGGIN[3] also found oxygen-containing organic compounds to be good solvents for heteropolyacids. The extraction of heteropolyacids has been reviewed by JEAN[4].

The extraction of heteropolyacids with oxygen-containing solvents has been applied to the determination of phosphorus, and to a lesser extent arsenic, germanium and silicon. Many colorimetric methods for phosphorus are based on the measurement of the absorbance of molybdophosphoric acid or its reduction product in an organic medium[5]. Attempts to make these methods selective have centred on control of pH and of concentration of reagents, selection of solvent mixtures and choice of reducing agents. Butyl acetate was recommended as a selective solvent for molybdophosphoric acid by KATO, OKINAKA AND OIZUME[6], but WADELIN AND MELLON[7] preferred a butanol–chloroform mixture which extracted less iron. PAUL AND POVER[8], who studied the extraction of molybdophosphoric acid with alcohols and esters, recommended *n*-butyl acetate or isobutyl acetate for the selective extraction of molybdophosphoric acid in the presence of molybdoarsenic acid. Recently[9], a spectrophotometric method has been described for the simultaneous determination of phosphorus, arsenic and germanium which makes use of successive extractions with isobutyl acetate and iso-octanol.

Colorimetric determination of molybdophosphoric acid has inherent disadvantages; there is evidence for more than one molybdophosphoric acid in solution, and FERRARI[10] considers that equilibrium exists between a yellow acid and a colourless one. The reduction product, "phosphomolybdenum blue", is also unsatisfactory for colorimetric analysis; BAMANN *et al.*[11] showed it to contain both $H_3PO_4 \cdot 10\ MoO_3 \cdot Mo_2O_5$ and $H_3PO_4 \cdot 8\ MoO_3 \cdot 2\ Mo_2O_5$.

Gravimetric methods of determining phosphorus as ammonium 12-molybdophosphate[12–14] and as organic-base 12-molybdophosphates[15] are more satisfactory, but interfering ions such as arsenate are often troublesome. Procedures for the removal of interfering ions are described in the British Standard method[16] for the determination of phosphorus in steel; some of these procedures are laborious. Although solvent extraction offers a method for separating molybdophosphate from interfering ions, its use as a preliminary to gravimetric determination has not been described.

EXPERIMENTAL

Reagents

Preparation of potassium dihydrogen phosphate solutions. Dried AnalaR potassium dihydrogen phosphate (0.128 g) and about 40 μC of the radioisotope phosphorus-32, as orthophosphate, were dissolved in 100 ml of water. An unlabelled solution containing 1.28 g of the salt/l was also prepared.

Preparation of disodium hydrogen arsenate solutions. Dried AnalaR disodium hydrogen arsenate heptahydrate (0.293 g) and about 40 μC of the radioisotope arsenic-74, as sodium arsenate, were dissolved in 100 ml of water. An unlabelled solution containing 2.93 g of the salt heptahydrate/l was also prepared.

Preparation of ammonium molybdate solutions. The reagent was prepared as described by THISTLETHWAITE[12]. Powdered AnalaR ammonium molybdate (35 g) was dissolved in 100 ml of aqueous 50% (v/v) ammonia. Concentrated nitric acid (168 ml, s.g. 1.42) was diluted to 360 ml with water and allowed to cool. The ammoniacal molybdate solution was poured into the nitric acid in a thin stream, with constant stirring. This solution was allowed to stand for 24 h, diluted to 900 ml with water, filtered, and stored in polythene containers. The radioisotope molybdenum-99, as ammonium molybdate, was added to the stock solution in some experiments.

Wash solutions. (*i*) *Acid ammonium nitrate.* A.R. ammonium nitrate (20 g) and nitric acid (12.5 ml, s.g. 1.42) were made up to 2.5 l with water.

(*ii*) *Nitric acid.* A 1% (w/v) solution was prepared.

Preparation of solutions containing transition-metal ions. Six solutions were prepared, each containing 1.28 g/l of dried potassium dihydrogen phosphate, and sufficient iron(III) nitrate to make Fe^{3+}/PO_4^{3-} ratios of 10, 25, 50, 75, 100 and 150 respectively. Solutions containing chromium(III) nitrate, manganese(II) nitrate and nickel(II) nitrate were prepared similarly.

Solvents. The organic solvents used for the liquid extraction were chosen to represent various types: alcohols, aldehydes, ketones, esters, ethers, hydrocarbons, halogenated hydrocarbons, and organic nitrogen compounds. "Laboratory Reagent" grade solvents were used. Some were fractionated before use but it was found that this treatment had no effect on their efficiency as extractants.

Radiochemicals. Phosphorus-32, arsenic-74 and molybdenum-99 were obtained as phosphate, arsenate and molybdate respectively, from The Radiochemical Centre, Amersham.

EXTRACTION STUDIES

The extraction of molybdophosphoric acid

Ammonium molybdate reagent (4 ml) was added to potassium dihydrogen phosphate solution (2 ml) containing about 0.5 μC phosphorus-32. Various solvents were used to extract molybdophosphoric acid by shaking 10 ml of solvent vigorously for 1 min with the aqueous solution. Preliminary experiments showed that shaking for 1 min was sufficient to allow equilibrium to be reached. The pH was adjusted with nitric acid or aqueous ammonia, and measured with an EIL direct-reading pH meter Type 23A, using a calomel electrode Type RJ 23 and a glass electrode Type GHS 23. To obtain values at pH < 2, a series of freshly-made solutions of equal strength were used instead of one solution, because slow precipitation occurs from acidic solution even at 20°. The distribution of phosphorus was calculated in each case from count-rates, corrected for self-absorption in the solvents, taken on the aqueous and organic phases in a Mullard MX 124 liquid counter with a Panax D 657 scaler.

Table I shows the optimum conditions for extraction with various solvents; chloro- and fluoro-hydrocarbons, higher ethers and esters, carbon disulphide, and amines except quinoline were poor extractants at 20°. Figures 1–3 show the complete extraction curves for some solvents at 20°.

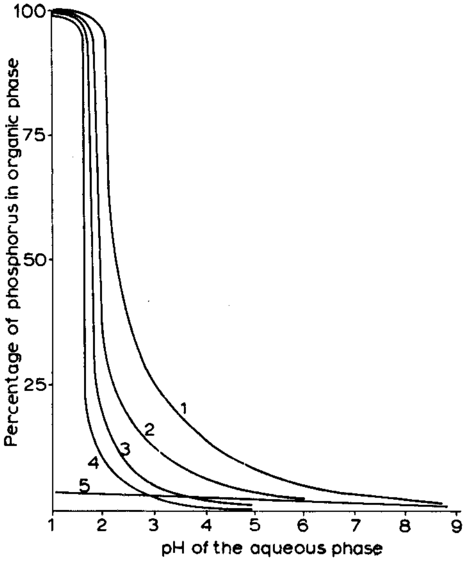
TABLE I

THE EXTRACTION OF PHOSPHORUS AS MOLYBDOPHOSPHORIC ACID AT 20°

Solvent	*Optimum conditions*		*Addition*	*P extracted into organic phase (%)*
	Nitric acid (M)	*pH*		
n-Butanol	1			99.9
Isobutanol		1.0		99.5
sec-Butanol		1.0		85.0
tert-Butanol		1.0	10 g $NaNO_3$	93.1
n-Pentanol	1			99.7
Isopentanol	1			99.8
n-Heptanol	1			99.5
Decanol	1			99.0
Cyclohexanol	1			99.4
Benzyl alcohol	1			99.3
Methyl acetate	1		10 g $NaNO_3$	74.4
Ethyl acetate	1			99.5
n-Propyl acetate	1			99.4
n-Butyl acetate	1			99.0
Amyl acetate	1			98.6
Cyclohexanone		4.0		99.3
Acetophenone	1			98.8
Benzaldehyde	1			98.2
Nitromethane	1			97.3
Quinoline		5.0		95.7
Pyridine	1		10 g $NaNO_3$	30.1

Experiments with labelled molybdate were done for some of the solvents. Ammonium molybdate reagent (4 ml) containing about 0.5 μC molybdenum-99 was added to potassium dihydrogen phosphate (2 ml); the distribution of molybdenum was calculated from corrected count-rates, taken in an IDL 663A counter, on organic and aqueous layers. Table II indicates the variation in the phosphorus/molybdenum ratio from one solvent to another. Experiments in the absence of phosphate showed that in the case of *n*-butanol, quinoline and cyclohexanone the amount of molybdenum extracted into the organic phase was only a few percent less than when the phosphate was also present.

Although these experiments with labelled molybdate suggest that the polyacid



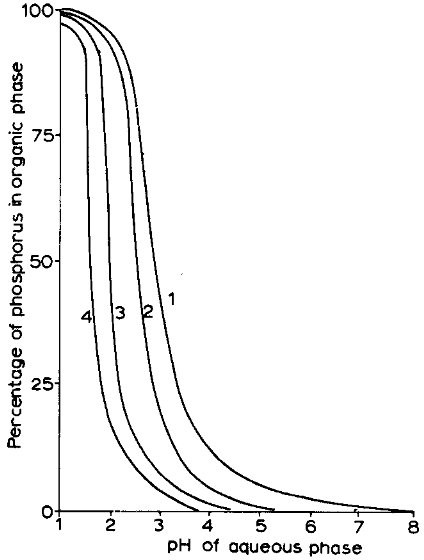
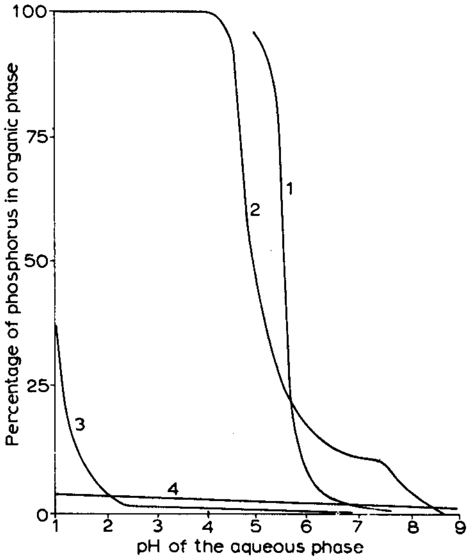


Fig. 1. The extraction of molybdophosphate with alcohols at 20°. Tracer: phosphorus-32. (1) *n*-butanol; (2) *n*-pentanol; (3) *n*-heptanol; (4) decanol; (5) extraction of phosphate with *n*-butanol. The Mo:P ratio in the aqueous phase originally was 42 (curves 1 to 4).

Fig. 2. The extraction of molybdophosphate with esters at 20°. Tracer: phosphorus-32. (1) ethyl acetate; (2) *n*-propyl acetate; (3) *n*-butyl acetate; (4) amyl acetate. The Mo:P ratio in the aqueous phase originally was 42.



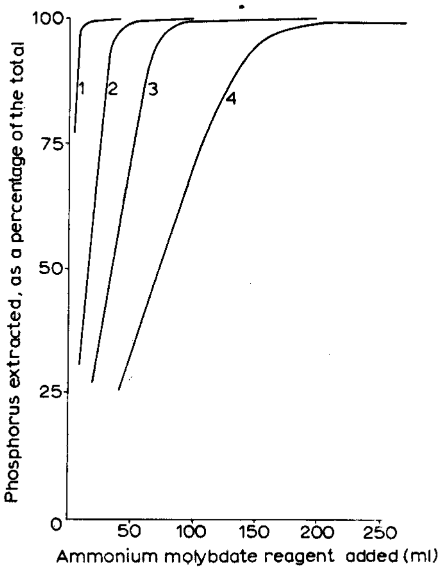


Fig. 3. The extraction of molybdophosphate at 20°. Tracer: phosphorus-32. (1) quinoline; (2) cyclohexanone; (3) diethyl ether; (4) extraction of phosphate with cyclohexanone. The Mo:P ratio in the aqueous phase originally was 42 (curves 1 to 3).

Fig. 4. The extraction of molybdophosphate with *n*-butyl acetate in the presence of iron. Tracer: phosphorus-32. (1) phosphorus extracted from a sample, 0.2 g containing 1.17% P, after formation of molybdophosphate at 20°; (2) phosphorus extracted from a sample, 0.5 g containing 0.12% P, after formation of molybdophosphate at 50°; (3) phosphorus extracted from a sample, 1 g containing 0.066% P, after formation of molybdophosphate at 50°; (4) phosphorus extracted from a sample, 5 g containing 0.006% P, after formation of molybdophosphate at 70°.

TABLE II

VARIATION IN Mo–P RATIO IN EXTRACT

Solvent	*Amount of ammonium molybdate added (Mo:P)*	*pH*	*P extracted into organic phase (%)*	*Mo extracted into organic phase (%)*	*Mo/P ratio in organic phase*
n-Butyl acetate	42	1.0	98.3	2.4	1.0
n-Heptanol	42	1.0	98.9	10.7	4.6
n-Butanol	42	1.0	99·9	28.6	12.0
Cyclohexanone	42	4·0	99·3	56.3	23·9
Quinoline	42	5·0	95·7	90·4	39·5

which is extracted may, and in some cases certainly does, contain less than 12 molybdenum atoms to each phosphorus, experiments on the extraction of labelled phosphate with butanol in the presence of different concentrations of molybdate showed that the excess of molybdate required to allow quantitative extraction of phosphorus was the same as that needed to precipitate a 12-molybdophosphate quantitatively—a molybdate/phosphate ratio of about 40.

Other experiments were made with mixed solvents such as butanol/chloroform and butanol/*n*-butyl ether, but in no case was extraction more efficient than with the pure solvent.

The re-extraction of molybdophosphate with dilute aqueous ammonia

Stepwise addition of aqueous ammonia was made to *n*-butanol extracts at 20°, and extraction coefficients were evaluated over the pH range 1–9 by measuring the count-rates given by the phosphorus-32 in the aqueous and organic layers. It was found that re-extraction of the phosphorus was complete at pH >9.

The extraction of molybdoarsenic acid with organic solvents

Ammonium molybdate reagent (4 ml) was added to disodium hydrogen arsenate solution (2 ml) containing about 0.5 μC arsenic-74. In experiments with different solvents under the same conditions as those on molybdophosphoric acid, the percentage of arsenic extracted by the organic solvent was found from the corrected count-rates. The results with representatives of 3 classes of solvents, alcohols, esters, ketones and also with quinoline, are shown in Table III.

TABLE III

THE EXTRACTION OF MOLYBDOARSENIC ACID AT 20°

Solvent	*Conditions*		*Stoichiometric ratio Mo/As*	*As extracted into organic phase (%)*
	pH	*Nitric acid (M)*		
n-Butanol		1	42	24·7
n-Pentanol		1	42	23.0
n-Heptanol		1	42	2.0
n-Propyl acetate		1	42	1.2
n-Butyl acetate		1	42	0.5
Cyclohexanone	2.0		42	97·9
Quinoline	5·0		12	92.5

Experiments were made with *n*-butanol to determine the effect of standing time and shaking time on the extraction of molybdoarsenic acid. Unlike molybdophosphoric acid, which could be extracted quantitatively on shaking for 1 min, the arsenic complex entered the organic layer slowly, and equilibrium (*ca.* 52% arsenic in the *n*-butanol layer) was not approached until the liquids had been intermittently shaken for more than 1 h.

The extraction of phosphate from solutions containing both phosphate and arsenate

The two solvents which seemed likely to be most satisfactory for the selective extraction of phosphate from solutions which also contained arsenate were, on the basis of the preliminary experiments, and consideration of cost and availability, *n*-butyl acetate and *n*-heptanol. In experiments designed to select the better of these solvents, ammonium molybdate reagent (4 ml) was added to radioactive potassium dihydrogen phosphate (2 ml), 1 *M* nitric acid (10 ml) and solvent (10 ml); the mixture was shaken for 1 min and the percentage of phosphorus extracted was found from corrected count-rates on 10-ml aliquots of the two phases. In some experiments inactive arsenate alone was used. Two successive extractions with 10 ml of either solvent were sufficient to extract the phosphate quantitatively, even in the presence of an equimolar concentration of arsenate, but *n*-butyl acetate extracted only 1.1% of the arsenate whereas *n*-heptanol extracted 4.2% of the arsenate (Table IV).

TABLE IV

RECOVERY OF MOLYBDOPHOSPHORIC AND MOLYBDOARSENIC ACIDS

(Equimolar solutions of arsenate and phosphate)

Solvent	*Phosphate present (ml)*	*Arsenate present (ml)*	*No. of extns. with 10-ml portions*	*P extracted (%)*	*As extracted (%)*
n-Butyl acetate	2	0	1	99.0	
	2	0	2	99.8	
	0	2	1		0.5
	0	2	2		1.1
	2	2	2	99.8	1.0
n-Heptanol	2	0	2	99.8	
	0	2	2		4.2

THE APPLICATION OF EXTRACTION WITH *n*-BUTYL ACETATE TO THE GRAVIMETRIC DETERMINATION OF PHOSPHORUS IN THE PRESENCE OF ARSENIC

The following general procedure was used except where otherwise stated.

Procedure

Ammonium molybdate solution was added to potassium dihydrogen phosphate solution. After acidification with 2 *M* nitric acid (2 ml), phosphorus was extracted by shaking with two 10-ml portions of *n*-butyl acetate for 1 min in each instance. The combined extracts were treated with two 10-ml portions of dilute aqueous ammonia; the ammoniacal extract was acidified with concentrated nitric acid (2 ml, s.g. 1.42) and added immediately to ammonium molybdate reagent (4 ml). This solution, which was stirred at 15-min intervals with a glass rod, was maintained at 50° for 1 h and for the same period at room temperature. The ammonium 12-molybdophosphate was collected in a sintered glass crucible of porosity 4, washed with acidic ammonium nitrate solution and given a final wash with 1% nitric acid solution. The precipitate was dried at 280° before weighing.

In the presence of transition-metal ions, it was found necessary to wash the organic extract with ammonium molybdate solution before re-extracting with ammonia; otherwise metal hydroxides were precipitated. Nitric acid and water were unsuitable wash liquids because both removed phosphorus from the organic phase, as shown by tracer experiments, the amount depending on the metal-ion/phosphate ratio.

In 6 experiments using 4 ml of ammonium molybdate and 2 ml of potassium dihydrogen phosphate solutions the mean weight of precipitate obtained was 35.4 mg (range 35.2–35.8 mg; theoretical yield of triammonium 12-molybdophosphate 35.3 mg).

The effect of arsenate

Ammonium molybdate solution (4 ml) was added to potassium dihydrogen phosphate (2 ml) and disodium hydrogen arsenate (2 ml). After extraction with *n*-butyl acetate, phosphorus was determined as above. The weight of the precipitate was not affected by the presence of arsenate equimolar with the phosphate.

When iron(III), chromium(III), nickel(II) and manganese(II) respectively were added as nitrates to (*a*) the phosphate solution alone, and (*b*) the equimolar phosphate/arsenate mixture, to give metal/phosphate ratios of 150 before addition of the molybdate, it was found that the weights of precipitates varied from 34.7 mg to 35.5 mg (mean 35.1 mg, theoretical weight 35.3 mg). Radiochemical measurements with phosphorus-32 showed that the recovery of phosphorus was in the range 98.2–99.5% (mean 99.0%).

THE DETERMINATION OF PHOSPHORUS IN STEEL

After trials with a range of iron and steel samples (kindly supplied by the Department of Metallurgy of this Faculty), a method was chosen for the gravimetric determination of phosphorus. "British Chemical Standard" samples of iron and steel were obtained from the "Bureau of Analysed Samples, Ltd.", and analysed by the method described below, which was adapted from the British Standard method[16].

Procedure

A weighed sample (see *Note*) was dissolved in a mixture of nitric acid (15 ml, s.g. 1.42) and hydrochloric acid (25 ml, s.g. 1.16) by heating in a covered flask. Perchloric acid (20 ml, s.g. 1.54) was added and the solution was evaporated to fumes. Heating was continued for 5 min at a temperature high enough to maintain a steady reflux of acid. The liquid was cooled, hydrochloric acid (10 ml, s.g. 1.16) and water (25 ml) were added, and the solution was then boiled for 5 min. Hydrochloric acid was not added at this stage to samples which were nominally free from chromium.

The solution was diluted to *ca.* 100 ml with water, and ammonium molybdate (Table V) and *n*-butyl acetate were added quickly. (For samples of low phosphorus

TABLE V

CHOICE OF SAMPLE WEIGHT AND CONDITIONS OF EXTRACTION WITH *n*-BUTYL ACETATE

P in sample (%)	*Original sample weight (g)*	*Aliquot taken from 100 ml of soln. (ml)*	*Amount of ammonium molybdate soln. required at the extn. stage (ml)*	*Temp. of precipitate formation (°)*
$<$ 0.02	5	100	200	70
0.02–0.1	2	100	100	50
0.1–0.4	1	50	70	50
0.4–0.8	1	25	50	50
$>$0.8	0.5	25	20	20

content, larger amounts of ammonium molybdate and higher temperatures were required; the ammonium molybdate and sample solutions were heated separately, and then mixed, along with the butyl acetate.) The flask was stoppered and shaken for 30 sec; if necessary the flask was cooled rapidly to room temperature with shaking and given a final shake for 30 sec. The extraction was always completed at room temperature. The lower aqueous layer was separated using a separating funnel and extracted with a further 50-ml portion of *n*-butyl acetate.

The combined organic extracts were washed with ammonium molybdate solution (50 ml) and the phosphorus was re-extracted with 2 successive portions of aqueous ammonia. The ammoniacal extract was filtered and the residue was washed several times with water. Nitric acid (6 ml, s.g. 1.42) and ammonium molybdate (10 ml) were added to the combined filtrate and washings. The digestion and gravimetric determination were then completed as described on p. 215.

Note. The sample weight was chosen to give a final precipitate weighing 20–100 mg, but to avoid errors from heterogeneity it was never less than 0.5 g. Where necessary, an aliquot of the dissolved sample was taken for further treatment. Table V shows the approximate weights of sample together with the extraction conditions used for a range of phosphorus contents. When an aliquot had to be taken, the solution of iron or steel was filtered and the residue washed with 0.2 *M* hydrochloric acid to remove adsorbed phosphate before dilution to 100 ml. Otherwise it was quite satisfactory, and also simpler, to use a single filtration just before the final precipitation of molybdophosphate.

The effects of temperature and time

The addition of ammonium molybdate at room temperature to the solution of iron or steel gave satisfactory extractions with samples containing more than 0.8% phosphorus. Quantitative extraction of lower percentages of phosphorus was impossible unless the solution was heated, but above 70° a white precipitate formed on addition of molybdate reagent; the reagent itself could be heated to 70° without decomposition provided that heating was slow and stirring continuous. The temperature required for the formation of molybdophosphoric acid depended on the Fe^{3+}/PO_4^{3-} ratio (Fig. 4). As butyl acetate did not extract the molybdophosphoric acid completely at high temperatures, the solution had to be cooled to room temperature to allow the extraction to be completed; rapid cooling minimised the amount of molybdoarsenic acid which was formed and extracted.

Radiochemical assays with phosphorus-32 showed that shaking for 1 min sufficed for extraction of 99% of the phosphorus. If the mixture of molybdate with iron(II) solution was allowed to stand for a few minutes before extraction, a precipitate began to form, but this did not happen if reasonable speed was used. The amount of molybdoarsenic acid produced and extracted increases with time but is only significant at high temperatures or if the organic and aqueous layers are left in contact for a prolonged period.

The effect of arsenic

Different amounts of active sodium arsenate were added to 1-g samples of high-purity iron and the percentage extraction under various conditions was investigated (Table VI). Several "British Chemical Standard" iron and steel samples were dissolved and active sodium arsenate was added; the solutions were extracted with *n*-butyl acetate under the conditions giving at least 99% extraction of phosphorus. After re-extraction into the aqueous phase, phosphorus was precipitated as ammonium 12-molybdophosphate; the percentages of the arsenic extracted into the organic layer and co-precipitated with the phosphorus were determined radiochemically (Table VII).

TABLE VI

THE EXTRACTION OF ARSENIC WITH *n*-BUTYL ACETATE UNDER THE CONDITIONS FOR QUANTITATIVE EXTRACTION OF PHOSPHORUS IN IRON AND STEEL (*cf.* TABLE V)

Amount of As added to 1 g of iron (mg)	*Amount of molybdate added (ml)*	*Temp. of formation (°)*	*As extracted (%)*
10	20	20	0.7
1	20	20	0.2
1	70	50	3.7
0.5	100	50	7.3
0.5	100	70	14.8
0.1	100	70	6.9

TABLE VII

THE PERCENTAGE OF ARSENIC EXTRACTED AND PRECIPITATED FROM SOME SPECIMENS OF IRON AND STEEL

BCS No.	*As content (%)*	*Amount of molybdate used in extn. (ml)*	*Formation temp. (°)*	*As extracted*[a]	*As precipitated*[a]
206/2[b]	0.035	20	20	0.4	< 0.1
		20	50	2.8	0.6
		20	70	7.0	1.7
		100	20	0.9	0.2
		100	50	4.2	0.9
		100	70	11.9	2.2
169	0.031	100	50	4.5	1.0
218/2	0.036	100	50	4.7	1.1

[a] Expressed as percentage of the arsenic content.

[b] A cast iron with high P and Si contents.

The effects of iron and chromium

Active potassium dihydrogen phosphate was added to high-purity iron and extracted with increasing amounts of ammonium molybdate and *n*-butyl acetate. Where the PO_4^{3-}/Fe^{3+} ratio was low, the temperature had to be raised for 99% extraction to be achieved (Fig. 4).

The precipitates of ammonium molybdophosphate obtained from steels containing more than 0.2% chromium were 10–30% too light, because of interference by dichromate. Boiling the acid solution of ferrous metal with hydrochloric acid, an adaptation from the British Standard method, removed the interference of chromium(VI), and the phosphorus was precipitated quantitatively.

The effect of tungsten

Active phosphate was added to a steel containing nearly 20% tungsten (B.C.S. No. 241/1). Samples were dissolved in the normal manner, without treatment of the tungstic acid residue, and two techniques for the extraction of phosphate were investigated.

(*i*) The whole solution, together with the tungstic acid residue, was extracted with ammonium molybdate and *n*-butyl acetate, and the phosphate extract was counted.

(*ii*) The tungstic acid residue was removed by filtration and washed several times with hot 0.2 *M* hydrochloric acid. The combined filtrate and washings were extracted by adding ammonium molybdate and *n*-butyl acetate, and the extract was counted.

In both cases the tungstic acid residue was ignited in a platinum crucible to dull red heat. The residue was cooled, a few drops of water, hydrofluoric acid (2 ml), and 5 drops of concentrated nitric acid were added, and the mixture was evaporated to dryness. The clear melt obtained by fusing with potassium bisulphate (3 g) was extracted with 15% tartaric acid (25 ml) and counted.

The percentage of phosphorus remaining in the residue extracted with *n*-butyl acetate was 0.2%. In the residue filtered after reduction of chromium, 5.9% of the phosphorus remained.

TABLE VIII

APPLICATION TO SOME "BRITISH CHEMICAL STANDARD" SPECIMENS OF IRON AND STEEL

BCS No.	*Sample*		*Special characteristics*	*Certified P content (%)*	*Radiochemical efficiency (%)*	*P found (%)*
149/2	High-purity iron		< 0.001% As	0.006	98.4	0.006
163/1	Carbon steel			0.026	98.9	0.026
169	Cast iron	2.26% Si	0.031% As	0.026	98.8	0.025
170/2	Foundry iron	2.53% Si		1.00	99.2	1.01
206/2	Cast iron	3.42% Si	0.035% As	1.37	99.3	1.37
218/2	Carbon steel		0.036% As	0.024	98.9	0.023
219/2	Ni–Cr–Mo steel	0.80% Cr	0.034% As	0.028	99.0	0.029
225/2	Ni–Cr–Mo steel	1.08% Cr		0.019	98.6	0.019
240/2	Carbon steel			0.025	98.7	0.024
241/1	High-speed steel	19.61% W		0.021	98.8	0.021
270	Carbon steel		0.03% As	0.092	99.2	0.090

Application of the method to metallurgical samples

Table VIII shows the results obtained when the procedure described was applied to B.C.S. samples of iron and steel.

DISCUSSION

Many oxygen-containing organic solvents can extract phosphorus, probably as molybdophosphoric acid, from acidic aqueous solutions containing phosphate and molybdate; the most useful are those containing 4–6 carbon atoms per molecule.

Molybdophosphoric acid is extracted by *n*-butanol even at pH 9 at room temperature; at pH 1, shaking for 1 min is enough to extract 99.9% of the phosphorus from an equal volume of aqueous solution provided that the Mo:P ratio is not less than 42. When this ratio is only 12 the extraction falls to 85.4%. The figure 42 is empirical and does not appear to have theoretical significance. Higher alcohols than butanol also extract molybdophosphoric acid, but with decreasing efficiency as molar mass increases. Esters such as propyl, butyl and amyl acetates are good extractants, but ethers are poor. Diethyl ether extracts only 40% of phosphorus under the conditions at which *n*-butanol extracts 99.9%. Cyclohexanone is a good extractant, especially at pH 4, and is comparable in efficiency with *n*-butanol. Compounds which do not contain oxygen are generally poor extractants. Exceptionally, quinoline extracts 95.7% of the phosphorus from an equal volume of an aqueous solution at pH 5; only quinoline and cyclohexanone extracted substantial amounts of phosphorus from very weak acid solutions. Experiments with mixtures of solvents did not reveal any synergistic effects.

An aqueous solution of phosphate and molybdate becomes yellow when acidified, and the yellow colour is transferred to the organic phase on shaking, but the complex is not necessarily the 12-molybdic acid. Tests with molybdenum-99 showed that the Mo:P ratio in the solvent was sometimes much greater than 12, but sometimes less. A complex containing an Mo:P ratio of 1 appeared to be extracted with *n*-butyl acetate at pH 1, even when the aqueous solution contained molybdenum and phosphorus in the ratio 42:1.

Many solvents which extract phosphorus also extract arsenic from acidic solutions, but they do so less readily. There is no common solvent which extracts molybdoarsenic acid but not molybdophosphoric acid.

The most useful solvent for effecting a separation of phosphate from arsenate is *n*-butyl acetate. Heptanol will also separate the two elements quite well, but it extracts a little more arsenic than does *n*-butyl acetate under the conditions which are best for quantitative extraction of phosphorus. Iso-octanol, which has recently been described as a good solvent for extracting phosphorus for spectrophotometric determination in the presence of arsenic[9], was unsatisfactory for gravimetric work because it was difficult to separate the layers cleanly.

Provided that the Mo:P ratio is 42 and the pH is not greater than 1, phosphorus can be extracted quantitatively by two extractions with *n*-butyl acetate. The amount of arsenate (equimolar with phosphate) extracted simultaneously is about 1%. Transition-metal ions inhibit the extraction of both phosphorus and arsenic. When the metal-ion/phosphate ratio is 150, two extractions with *n*-butyl acetate remove 98–99.5% of phosphorus, depending on whether Fe^{3+}, Cr^{3+}, Ni^{2+} or Mn^{2+} is present.

In the presence of iron and phosphate, the extraction of arsenic falls to 0.3%. Transition-metal ions are extracted with *n*-butyl acetate, but they can be stripped by washing with aqueous ammonium molybdate, which does not re-extract the phosphorus.

After the primary separation of phosphorus and arsenic with *n*-butyl acetate, the molybdophosphoric acid complex can be destroyed with aqueous ammonia and the phosphorus re-extracted into the aqueous layer. Ammonium 12-molybdophosphate can be precipitated quantitatively from the acidified aqueous solution at 50° and the phosphorus thus estimated gravimetrically as $(NH_4)_3PMo_{12}O_{40}$. The method is not affected by the many variables which affect the classical colorimetric methods. The small amounts of arsenic that are extracted with *n*-butyl acetate give only trace amounts of ammonium molybdoarsenate under the conditions used.

Solvent extraction with *n*-butyl acetate can be adapted to the determination of phosphorus in iron and steel. After the dissolution process, molybdophosphoric acid is formed at a temperature between 20° and 70° depending on the type of sample. The solution and any solid residue it contains are extracted twice with *n*-butyl acetate at room temperature; a residue which contains zirconium has to be treated as described in the British Standard method[16], however, as zirconium phosphate is insoluble under the conditions of the extraction.

The combined extracts are washed with aqueous ammonium molybdate to remove metal ions, and then shaken with aqueous ammonia to destroy the complex; the phosphorus can then be precipitated as ammonium 12-molybdophosphate from the aqueous extract, which now contains very small amounts of interfering ions. If the temperature of precipitation is kept below 50°, only trace amounts of arsenic are co-precipitated.

The choice of conditions for the formation of molybdophosphoric acid before extraction depends on the phosphorus content of the sample; a formation temperature as high as 70° and a large excess of ammonium molybdate is necessary for samples containing $< 0.02\%$ phosphorus, but there are very few steels of this type which contain significant amounts of arsenic, and very little molybdoarsenic acid is therefore extracted even after such extreme treatment. Since *n*-butyl acetate does not extract molybdophosphoric acid easily above 50°, solutions have to be cooled, but this cooling has the advantage of hindering the formation of the slowly produced molybdoarsenic acid.

Although the method requires large quantities of molybdate, they are no larger than those used in the British Standard method[16] or in the quinolinium molybdate method of LENCH[15]. Samples of iron containing 1% phosphorus can be extracted at room temperature using a much smaller excess of molybdate than is necessary for other methods.

The results obtained for a variety of British Chemical Standard samples of iron and steel agree well with values obtained by the British Standard method. The proposed method has the advantage for samples which contain significant amounts of arsenic that it is quicker and does not require the use of hydrobromic acid, which may itself contain some phosphorus.

SUMMARY

The radioisotopes phosphorus-32 and arsenic-74 have been used to study the extraction of molybdophosphoric and molybdoarsenic acids from aqueous solution with various organic solvents. A method is described for the gravimetric determination of phosphorus in the presence of arsenic which makes use of solvent extraction with *n*-butyl acetate. The results obtained for the determination of phosphorus in various types of iron and steel are described.

RÉSUMÉ

Les radioisotopes phosphore-32 et arsenic-74 sont utilisés pour étudier l'extraction des acides molybdophosphorique et molybdoarsénique à l'aide de divers solvants organiques. On décrit une méthode de dosage gravimétrique du phosphore en présence d'arsenic, avec extraction dans un solvant le *n*-butylacétate. On donne les résultats obtenus pour le dosage du phosphore dans divers types de fer et d'acier.

ZUSAMMENFASSUNG

Mit den Radioisotopen Phosphor-32 und Arsen-74 wurde die Extraktion der Molybdophosphor- und Molybdoarsensäuren aus wässriger Lösung mit verschiedenen organischen Lösungsmittlen untersucht. Zur gravimetrischen Bestimmung von Phosphor in Gegenwart von Arsen wird eine Methode beschrieben, die als Extraktionsmittel *n*-Butylacetat verwendet. Die Ergebnisse, die für die Bestimmung von Phosphor in verschiedenen Typen von Eisen und Stahl erhalten wurden, werden beschrieben.

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CHEMICAL DETERMINATION OF SOME MAJOR CONSTITUENTS IN ROCKS AND MINERALS

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Since the publication of WASHINGTON's work[1] in 1919 his classical procedure for the chemical analysis of silicate rocks has been widely employed. More recently, other analytical schemes have been devised, particularly spectrophotometric methods, for the determination of the minor constituents in rocks. Although these procedures increase the rapidity with which major constituents can be determined, they rarely lead to improved precision.

The value of the classical scheme has been broadly recognised over the years, but various shortcomings have been noted, particularly in the determination of aluminium. The lack of a suitably precise method for this geochemically important element led to the present investigation, which was later extended to a study of available methods for some other major constituent elements in rocks (*e.g.*, total iron, iron(II), calcium and magnesium).

Aluminium

In the classical procedures[1,2] aluminium is determined by difference from the weight of the ignited ammonia precipitate (R_2O_3) after all other elements have been determined individually. The aluminium result is, therefore, greatly dependent on the accuracy with which the other elements in the precipitate can be determined and the error is clearly evident in the analysis of materials with low Al/Fe ratio. This procedure has been improved[3] by passing a hydrochloric acid solution of the group precipitate through an anion-exchange column; iron is retained and aluminium passes through the column, accompanied by titanium, chromium, nickel, a variable amount of manganese and traces of iron. Aluminium can then be determined gravimetrically and the elements following the aluminium are determined spectrophotometrically; a correction is applied, which inevitably again introduces experimental errors.

PŘIBIL AND VESELÝ[4] were able to separate titanium and iron from aluminium in a ternary system by precipitating titanium with sodium hydroxide in the presence of triethanolamine (TEA). Iron and titanium were also separated by precipitating with cupferron[5] (ammonium salt of N-nitrosophenylhydroxylamine) and subsequent removal by chloroform extraction. In the present work, initial experiments were conducted with a solution containing aluminium, iron and titanium by applying these separation techniques. In addition, methyl isobutyl ketone (MIBK) was used to extract large quantities of iron and 2,2'-dipyridyl was used to mask residual traces of iron. Aluminium was then precipitated and ignited to the oxide in the usual way. Based on these principles of isolation, several standard rocks were analysed. Iron, titanium and phosphorus were determined in the ignited alumina spectrophotometrically. The results, however, tended to be high (Table I). This procedure is complicated and offers no advantage over the anion-exchange separation.

TABLE I

ISOLATION OF ALUMINIUM FOR GRAVIMETRIC DETERMINATION

Rock type	*Aluminium (as % Al_2O_3)*		*Contaminants found (p.p.m.)*
	Accepted values	*This work*	
NBS 1a Limestone Standard	4.16	4.65	Fe_2O_3 = 9000 TiO_2 = Nil P_2O_5 = 8610
USGS BCR-1, (44/20) Basalt Standard	13.63[a]	13.89	Fe_2O_3 = 3200 TiO_2 = Nil P_2O_5 = 7350
W-1 Diabase Standard	14.48–15.74[b] (Mean = 15.06)	15.66	Fe_2O_3 = 10000 TiO_2 = 36.5 P_2O_5 = 1930
USGS AGV-1, (28/12) Andesite Standard	17.10[c]	17.22	Fe_2O_3 = Nil TiO_2 = Nil P_2O_5 = Nil

[a] Analysed by VERTIE C. SMITH[17].
[b] Limits of Acceptance, Geological Survey Bulletin 1113.
[c] Analysed by ELAINE L. MUNSON[17].

Other methods of separation and determination of aluminium were studied with special attention to compleximetric titrations. The reaction of aluminium with EDTA is slow and boiling is essential to complete chelation. The aluminium–EDTA reaction is not entirely stoichiometric and is influenced by the salt concentration of the solutions. Despite these shortcomings, PŘIBIL AND VESELÝ[6] were able to develop a significantly improved method for the determination of aluminium with EDTA: after the quantitative precipitation of titanium as hydroxide, aluminium and iron were reacted with an excess of EDTA on boiling; after back-titration, aluminium was determined directly by displacing EDTA from the aluminium chelate by boiling with ammonium fluoride. In the present work, a modification of this procedure was employed for the determination of aluminium in a number of standard rocks and other materials, which were brought into solution by evaporation with hydrofluoric–sulphuric acid evaporation, or by sodium carbonate fusion. Iron and titanium were separated by (*a*) sodium hydroxide precipitation of titanium in the presence of TEA; (*b*) MIBK extraction of iron followed by cupferron/chloroform extraction of titanium, or (*c*) cupferron/chloroform extraction of iron and titanium. Unfortunately, the results for aluminium showed a significant scatter, probably because of salt effects. For example, with W-1 Diabase Standard the mean result of 7 determinations was 14.98% Al_2O_3 with an average deviation from the mean of ±0.145%. This compares unfavorably with the results shown in Table II and further tests were therefore abandoned.

PŘIBIL AND VESELÝ[7] have shown that aluminium forms a stable chelate with *trans*-1,2-diaminocyclohexanetetraacetic acid (DCTA); the reaction is stoichiometric and very rapid even in the cold. As with EDTA, DCTA is not selective, hence nearly all elements except alkali and alkaline earth metals must be separated; large concentrations of neutral salts can be tolerated. The determination of aluminium with DCTA has been recommended by various workers[8–10]. MERCY AND SAUNDERS[10] have recently published a critical study on the precision and accuracy of aluminium and iron determinations in the chemical analysis of silicates, in which titration with DCTA is favoured for its precision. In the present work, several procedures were tested for the separation of interfering elements before the titration with DCTA. Efficient extractions of iron and titanium were obtained by the following techniques: (*a*) pre-extraction of iron with MIBK followed by cupferron/chloroform extraction of titanium; (*b*) simultaneous extraction of iron and titanium with cupferron/chloroform.

The former two-step extraction permitted the determination of aluminium, iron and titanium from one aliquot. The latter extraction was both efficient and rapid. The aqueous phase containing aluminium, manganese, chromium and nickel was evaporated in the presence of perchloric acid and nitric acid and chromium was volatilised as chromyl chloride by adding hydrochloric acid to a hot perchloric acid residue of the sample. Aluminium was then complexed with an excess of DCTA at pH 3.5, the excess being back-titrated with lead nitrate at pH 5.0–5.5 with xylenol orange as indicator. Manganese and nickel were quantitatively co-titrated and corrections were necessary. Vanadium in the metamorphic and more basic rocks (up to 800 p.p.m. V) was not extracted by the cupferron/chloroform process; its effect was overcome by treatment with hydrogen peroxide before the back-titration.

Total iron as Fe_2O_3

In the classical procedures[1,2] total iron is determined by titration with permanganate of an aliquot of the R_2O_3 precipitate after pyrosulphate fusion. The main source of error is that some iron alloys with the platinum crucible.

Spectrophotometric determination of iron has been widely employed in silicate analysis, based on such well-known reagents as 2,2′-dipyridyl, 1,10-phenanthroline and thioglycollic acid. These methods offer sufficient precision for rocks and minerals containing only minor proportions of this element, but where iron is a major constituent, dilution errors may be appreciable. It was felt, therefore, that an alternative method for macro-quantities of iron was desirable for better accuracy.

Direct titration of iron(III) with EDTA was unsuitable because of the indistinct end-point detection. PŘIBIL AND VESELÝ[6] described an indirect method based on the back-titration of an excess of EDTA with bismuth, thorium and lead using xylenol orange as indicator. This method is capable of high precision with advantages in its application to silicate rock analysis. In the present work, near specificity and freedom from interference was achieved by means of liquid–liquid extraction of iron. Extraction of the chloroferrate anion from 7 *N* hydrochloric acid with MIBK[11] was found very satisfactory. Iron was quantitatively recovered from the organic phase by shaking with water. The nearly selective extraction of iron from a multicomponent silicate rock solution offers an elegant method for the separation of other constituents.

Iron(II)

In the classical determination of iron(II) in silicate rocks, titration with permanganate after hydrofluoric/sulphuric acid dissolution is most commonly employed[2].

More recently, spectrophotometric methods have been used and RILEY AND WILLIAMS[12] have devised a micro-analytical method; the finely ground sample (1–5 mg) is dissolved in hydrofluoric/sulphuric acid mixture under nitrogen and the iron(II) is determined spectrophotometrically with 2,2′-dipyridyl. This method is valuable for the determination of the oxidation state of iron in high pressure and temperature experiments involving a few milligrams of silicate rock[13]. Although good precision was obtained by this method for FeO-contents up to 15%, higher iron(II) contents gave unsatisfactory results.

In the present work, a macro method was developed for the determination of iron(II) in silicates and minerals. An all-"Teflon" digestion apparatus was constructed for the sample digestion. Steam bath heating was used and a flow of pure nitrogen provided an inert atmosphere as well as stirred the mixture. Finely ground sample was digested with hydrofluoric/sulphuric acid mixture and the solution was titrated potentiometrically with dichromate solution; the potential was continuously recorded, and the equivalence point was obtained graphically. Under the conditions of the titration, both barium diphenylamine sulphonate and ferroïn indicators gave slow responses and therefore erroneous values.

Calcium and magnesium

The classical analytical scheme employs double ammonia precipitation of the R_2O_3-group before the precipitation of these elements[2]; this method is efficient but time-consuming. The common interfering elements (*e.g.*, iron, aluminium, titanium and manganese) may be conveniently separated by chelation with 2,4-pentanedione (acetylacetone)[14] at pH 6–7 followed by extraction with carbon tetrachloride. After the oxidation of the excess ketone, calcium and magnesium may be determined by conventional gravimetric methods or by titration with EDTA. Magnesium-tolerance of Acid alizarin black SN is satisfactory and this is a suitable indicator for the titration of calcium with EDTA[15]. Calcium and magnesium may be titrated with EDTA using xylenol orange as indicator in alkaline medium in the presence of micelle-forming cationic detergents such as cetylpyridinium bromide[16].

EXPERIMENTAL

Apparatus

pH was measured with a PYE Model 605 pH-meter and glass-calomel electrode system. Potentials were measured using a platinum/tungsten bimetallic electrode.

Reagents

Double de-ionised water and "Pyrex"-distilled water were used for all solutions. "AnalaR"-grade chemicals were used unless stated otherwise. Methyl isobutyl ketone was B.D.H. Laboratory Grade.

Hydrofluoric–sulphuric acid mixture. Add 40 ml of concentrated hydrofluoric acid to 60 ml of 5 *N* sulphuric acid. Saturate this mixture with nitrogen before use.

Nitric–perchloric acid mixture. Add 75 ml of concentrated nitric acid to 25 ml of concentrated perchloric acid.

Cupferron–chloroform reagent. (Prepare immediately before use.) Dissolve 6 g of ammonium N-nitrosophenylhydroxylamine in 100 ml of ice-cold water. Filter into a 250-ml separating funnel, add 6 ml of concentrated hydrochloric acid and shake. Extract the free base with 100 ml of ice-cold chloroform and filter the extract into a beaker. Repeat the extraction with another 100 ml of ice-cold chloroform and filter into the same beaker. Mix well and keep the reagent on crushed ice (or in a dry ice/alcohol bath at $-5°$) during use. Discard if any brown coloration appears.

Standard solutions

Potassium dichromate, 0.0139 N (1 ml ≡ 1 mg FeO). Dry the finely ground substance at 120° for 2 h. Weigh 0.6826 g, dissolve and dilute to 1000 ml. Standardise against "Specpure" iron(II) sulphate heptahydrate exactly as described for the macro-scale determination of iron(II) in rocks.

DCTA, 0.02 M. Suspend 7.5 g of *trans*-1,2-diaminocyclohexanetetraacetic acid (K & K Laboratories, Inc., Plainview, N.Y., U.S.A.) in about 200 ml of water and add 20% sodium hydroxide dropwise until a clear solution is obtained. Dilute to 1000 ml. Standardise against 0.02 *M* lead nitrate in a hexamine-buffered medium at pH 5–5.5 using xylenol orange as an indicator; better standardise against "Specpure" ammonium aluminium sulphate dodecahydrate, as described in Method A.

EDTA, 0.02 M. Standardise against lead nitrate solution as described above or better, against "Specpure" iron(III) oxide as described in Method C. If lead nitrate is used as the standard, it should be dried at 120° for 2 h and stored in a desiccator.

Determination of aluminium

(A) Materials decomposed by hydrofluoric acid. Weigh 0.5–1 g of finely ground material (100–150 mesh BSS) into a 100-ml platinum evaporating dish. Add 30 ml of water cautiously and 6 ml of 50% sulphuric acid. Stir the suspension with a platinum wire and add 40 ml of concentrated hydrofluoric acid. Evaporate to near dryness on a boiling water bath while stirring the contents frequently. Cool and add 10 ml of concentrated hydrofluoric acid when the dissolution acquires a greenish tint. Evaporate on a water bath and continue heating on a hot plate until strong fumes of sulphuric acid evolve. Cool and add 50 ml of water. Evaporate on a water bath to incipient crystallisation. Add some water again and dissolve salts by heating. Transfer the contents to a 500-ml volumetric flask and dilute to the mark. (The white precipitate or opalescence due to calcium sulphate will clear in an hour or so.) This solution is used for the determination of aluminium, calcium, magnesium and all the minor constituents as required.

Carry out the aluminium determination at least in duplicate. Pipet an aliquot equivalent to 100–200 mg of sample into a small beaker and add 5 ml of saturated bromine water. Evaporate until only a few ml of the solution is left. Add 10 ml of 7 *N* hydrochloric acid and warm the contents gently. Transfer the cold solution to a 125-ml separating funnel and wash the beaker with the 7 *N* acid quantitatively. Add 30 ml of MIBK, shake vigorously for 1 min and drain the acid layer to the beaker used previously. Shake the organic extract with five 5-ml portions of 7 *N* hydrochloric acid and add the rinses to the beaker. Reserve the organic extract for the determination of iron.

Evaporate the contents of the beaker to about 1–2 ml and add 15 ml of 1 *N* hydrochloric acid. Transfer the solution to a 125-ml separating funnel and wash the beaker quantitatively with the 1 *N* acid. Extract titanium with 10 ml of cupferron–chloroform reagent by shaking vigorously for 1 min. (If insufficient sample is available and the titanium content is required, the organic phase may be saved.) Repeat the extraction with 5 ml of the extractant until the bright green colour of the titanium complex changes to the dull green colour of the reagent. Remove excess of cupferron by shaking with 3 × 5 ml of 1:9 chloroform–acetone mixture. Drain into a 250-ml tall-form beaker and wash the funnel at least 5 times with water. Evaporate the solution to about half its original volume and add 10 ml of nitric–perchloric acid mixture. Continue boiling until perchloric acid fumes are apparent. If chromium is present, add 5 ml of concentrated hydrochloric acid dropwise to the slightly cooled solution and boil down to strong fumes. Cool when incipient crystallisation is observed. Add 5 ml of 1 *N* nitric acid and warm a little. Then add 10 ml of water and dissolve salts by heating, if necessary. Adjust the pH to 3.5 by dropwise addition of saturated aqueous hexamine solution, using a pH meter. Stir the solution magnetically with a PTFE-coated bar. Add an excess of 0.02 *M* DCTA solution to give a back-titration of 10–15 ml. Adjust the pH to 5.0–5.5 by further addition of hexamine buffer solution. Add 3–4 drops of 0.2% xylenol orange indicator in 50% ethanol and titrate with 0.02 *M* lead nitrate to an intense red colour. Any manganese and nickel present will be quantitatively co-titrated. Under these conditions of separation it is necessary to make the following calculations: 1 ml 0.02 *M* DCTA ≡ 1.0196 mg Al_2O_3, or 1.4188 mg MnO, or 1.4942 mg NiO. If vanadium is present in more than trace amounts, add 2 drops of 30% hydrogen peroxide to the buffered solution before the addition of xylenol orange indicator.

(B) Materials not readily attacked by hydrofluoric acid. Weigh out 0.5–1 g of finely ground material (100–150 mesh BSS) and mix with 7–8 g of anhydrous sodium carbonate in a medium platinum crucible. Fuse the mixture on a moderate heat with a Meker burner. Increase the heat, when the effervescence ceases, to *ca.* 900° for 5 min. (More vigorous fusion may be obtained by using a 9:1 mixture of sodium carbonate and sodium nitrate. More resistant materials should be fused with sodium peroxide in a zirconium crucible.) Leach out the fusion cake, acidify with hydrochloric acid and dehydrate the solution as recommended for the conventional silica determination. After ignition, expel silica by hydrofluoric acid evaporation, fuse the ignited residue with sodium pyrosulphate (not with potassium pyrosulphate) and add the leached fusion to the silica filtrate. Carry out the double ammonia precipitation and reserve the filtrate for determination of calcium and magnesium. Dissolve the ammonia precipitate in hydrochloric acid and evaporate to near dryness. Add 30 ml of 7 *N* hydrochloric acid and transfer the solution to a 250-ml separating funnel. Wash the beaker quantitatively with 7 *N* hydrochloric acid and add 80 ml of MIBK. Shake vigorously for 2 min. Drain the acidic layer to a 400-ml tall-form beaker and shake the organic extract with five 10-ml portions of 7 *N* hydrochloric acid. Add these washings to the beaker. Reserve the organic phase for the determination of total iron.

Evaporate the contents of the beaker to about 10 ml, add 10 ml of saturated bromine water and evaporate to about 5 ml. Avoid dehydration as loss of aluminium may result. Cool and transfer the solution to a 250-ml separating funnel. Wash the beaker with 1 *N* hydrochloric acid and extract titanium with cupferron–chloroform reagent (Method A). Remove any chromium present as in Method A. Add 5 ml of 1 *N* nitric acid to the chloride-free residue and dilute to 250 ml. Titrate aliquots exactly as recommended in Method A.

In certain cases where no iron determination is required, the separation technique may be greatly simplified by extracting titanium and iron simultaneously from 1 *N* hydrochloric acid solution using the cupferron–chloroform reagent. The

TABLE II

TYPICAL RESULTS OF ALUMINIUM AND IRON DETERMINATIONS

Rock type/mineral type	*Aluminium (as % Al_2O_3)*		*Total iron (as % Fe_2O_3)*	
	Accepted values	*This work*	*Accepted values*	*This work*
USGS PCC-1, (71/4) Peridotite Standard	0.74[a]	0.72 0.74	8.29[a]	8.28 8.29
G-1 Granite Standard	13.95–14.69[b]	14.15±0.036[c] (10 detns.)	1.76–2.32[b] (Mean 1.94)	1.83 1.88 1.82
W-1 Diabase Standard	14.48–15.74[b]	15.10±0.036[c] (8 detns.)	10.94–11.50[b] (Mean 11.13)	11.00, 11.05 11.01, 11.05
NBS 99 Soda-Feldspar Standard	19.06	18.96±0.015[c] (4 detns.)	—	—
NBS 69A Bauxite Standard	55.0	54.50±0.08[c] (4 detns.)	—	—
Eclogite, No. 2520 (Almklavdalen, Norway)	—	15.79±0.06[c] (6 detns.)	—	12.08, 12.11
Eclogite, No. 2607 (Kimberley, South Africa)	—	11.08 11.12	—	12.11, 12.12
Eclogite, No. 2628 (Kimberley, South Africa)	—	14.66 14.66	—	12.27, 12.24
Garnet, ex Eclogite No. 2832	—	—	—	33.87, 33.88
Hornblende, G 107, ex Quartz-diorite (Yeoval, N.S.W., Austr.)	—	4.81 4.83	—	17.97, 18.02
Hornblende, Y 161, ex Quartz-diorite (Yeoval, N.S.W., Austr.)	—	5.72 5.79	—	17.98, 18.02
Hornblende, Y 227, ex Quartz-diorite (Yeoval, N.S.W., Austr.)	—	4.56 4.56	—	17.97, 17.99
Muscovite, ex Eclogite No. 2520 (Almklavdalen, Norway)	—	27.02±0.03[c]	—	— —

[a] Analysed by VERTIE C. SMITH[17].
[b] Limits of Acceptance, Geological Survey Bulletin 1113.
[c] Mean result ± average deviation from mean.

extraction procedure is identical with that for titanium. Corrections for the co-titrated manganese and nickel are also applicable (see above).

Standard rocks and other materials containing 0.7–55% Al_2O_3 were analysed. The results are listed in Table II; it can be seen that both the reproducibility and the agreement with accepted values are satisfactory.

Determination of total iron as Fe_2O_3

(C) Materials decomposed by hydrofluoric acid. Shake the MIBK extract reserved in Method A with 10 ml of water for 1 min. Drain the separated aqueous layer to a 250-ml Erlenmeyer flask containing 1 ml of 7 *N* hydrochloric acid. Wash the extract with five 5-ml portions of water and add to the flask. Heat the contents of the flask gently at first, then boil to remove organic vapours and cool. Add *ca.* 10 mg of sulphosalicylic acid and sufficient 0.02 *M* EDTA to discharge the red colour. Then add an excess of EDTA to give a back-titration of 10–15 ml. Adjust the pH to 5.0–5.5 by drop-wise addition of saturated aqueous hexamine solution; use a strip of narrow-range indicator paper. Warm on a hot plate to about 60° and cool somewhat. Add 4–5 drops of 0.2% xylenol orange indicator in 50% ethanol and titrate with 0.02 *M* lead nitrate. The end-point is very sharp even in the presence of much iron. High iron concentrations give a dichroic effect but the end-point is unmistakable and the titrations are closely reproducible.

(D) Materials not readily attacked by hydrofluoric acid. Extract the total iron(III) which was derived from the ammonia precipitate (Method B) by shaking the MIBK extract with 50 ml of water. After the phase separation, drain the aqueous layer to a 250-ml beaker. Repeat the back-extraction with two 50-ml portions of water and two 10-ml portions of water. Heat the combined extracts slowly in order to expel organic matter. Increase the temperature to boiling when the solution is clear, and continue boiling until *ca.* 50 ml remains. Cool and transfer to a 250-ml volumetric flask. Add 25 ml of 1 *N* hydrochloric acid and dilute to the mark. Pipet aliquots equivalent to 100–200 mg of sample into 250-ml Erlenmeyer flasks and titrate as recommended in Method C.

Some total iron determinations are listed in Table II.

Determination of iron(II)

A special PTFE-digestion apparatus was constructed (Fig. 1), which was also designed to be used as a titration cell under constant nitrogen flow. The digestion vessel was connected to a pure nitrogen supply. (Commercial grade "Dry Nitrogen" was scrubbed with a 15% (v/v) pyrogallol solution in 50% potassium hydroxide in an acrylic vessel of cylindrical shape.) The manifold of the nitrogen supply was provided with a condensate trap and an outlet for the reagents. The rate of heat-transfer of the PTFE-digestion apparatus of the wall-thickness specified was determined. The temperature inside the vessel filled with water rose to a maximum of 80° 10 min after immersion in a boiling water bath. This temperature appeared to be constant and sufficed to decompose most materials; heating tape coupled to a thermostat could be used to produce internal temperatures up to 100°. The digestion apparatus could be converted to a pressure vessel operated at a maximum of 200° by constructing two needle valves consisting of PTFE components; all but the most refractory minerals can then be decomposed.

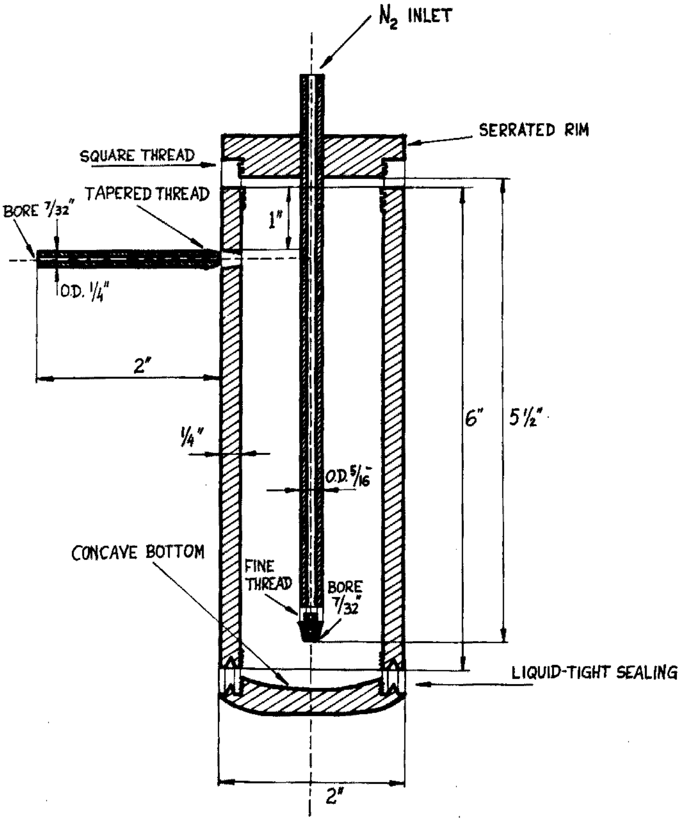

Fig. 1. Teflon digestion apparatus.

Procedure. Weigh 0.05–0.50 g of finely ground material (240 mesh BSS) into the digestion apparatus. (PTFE vessels should never be rubbed because the electrostatic charge accumulated may scatter the sample.) Wash the wall of the apparatus with *ca.* 5 ml of water saturated with nitrogen. Swirl the contents to obtain an even suspension. Depending on the weight of the sample taken, add 10–30 ml of hydrofluoric–sulphuric acid mixture and swirl the contents again. Close the top of the apparatus promptly and connect the nitrogen supply. Adjust the nitrogen inlet PTFE tube to lie about 0.25 in above the bottom of the vessel. Connect the outlet of the digestion apparatus to a cylinder half-filled with a weak potassium hydroxide solution. Immerse the digestion apparatus for 60 min in a boiling water bath and adjust the nitrogen flow to 2–4 bubbles per sec. Withdraw the digestion apparatus, open the top and rinse down all condensed droplets with water saturated with nitrogen. Pull up the threaded lid as far as it can go, and, maintaining constant nitrogen flow, transfer to a titration stand. Adjust the nitrogen flow to give moderately fast stirring. The final volume of the solution may be 80–100 ml. Immerse the bimetallic electrode (Fig. 2). Record the initial mV value, and titrate with the standard potassium dichromate solution.

Typical results are listed in Table III.

The response of the bimetallic electrode gradually diminishes in routine use

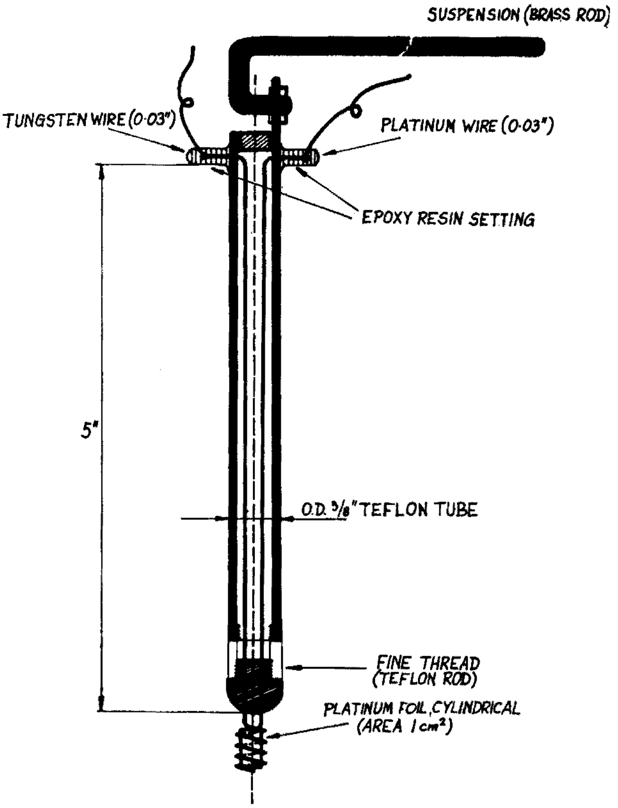

Fig. 2. Platinum–tungsten bimetallic electrode in teflon-housing.

because of the formation of a thin oxide film on the tungsten wire. The electrode system can be restored to full response by dipping the tip in molten sodium nitrite for 1–2 sec, after which it is equilibrated in distilled water.

Extraction of interfering elements before determination of calcium and magnesium

Transfer an appropriate aliquot (150–200 ml) of the stock solution (Method A) to a 250-ml or a 500-ml separating funnel. Add 30 ml of a 5% solution of freshly distilled 2,4-pentanedione in carbon tetrachloride and shake vigorously. Adjust the pH to 6–7 by addition of 1:1 ammonium hydroxide (narrow-range indicator paper). Shake vigorously for 1 min and discard the organic layer. Repeat the extraction with 10 ml of reagent. Shake the aqueous phase with 10 ml of carbon tetrachloride and discard; scrub with further portions of carbon tetrachloride until no yellow colour remains. Acidify to pH 3 with concentrated hydrochloric acid and extract with 15 ml of carbon tetrachloride. Add 5 ml of saturated bromine water, mix for 1 min and add sodium sulphite until the bromine colour just disappears. Drain the contents of the funnel into a 400-ml tall-form beaker and wash the funnel 6–7 times with water. Remove the residual solvent by careful heating. The entire separation process takes only 10 min and the aliquot may then be processed for the determination of calcium and magnesium by any preferred method.

TABLE III

DETERMINATION OF IRON(II) BY POTENTIOMETRIC TITRATION

Rock type/mineral type	*Iron(II) as % FeO*		
	Accepted values	*Others*	*This work*
G-1 Granite Standard	0.89–1.10[a]	—	0.90 0.91
ASG-1 Granodiorite Standard	—	4.39[b] 4.46[c] 4.47[d]	4.30 ± 0.017
W-1 Diabase Standard	8.22–9.04[a]	8.80	8.75 ± 0.045
USGS BCR-1, (44/20) Basalt Standard	9.09[d]	—	8.94 8.92
Eclogite, No. 2520 (Almklavdalen, Norway)	—	—	9.46 9.43
Eclogite, No. 2607 (Kimberley, South Africa)	—	—	8.35 8.39
Eclogite, No. 2627 (Kimberley, South Africa)	—	—	10.03 10.05
Eclogite, No. 2628 (Kimberley, South Africa)	—	—	8.90 8.85
Magnetite, D 33266 (Pt. Henry, Essex County, N.Y., U.S.A.)	—	30.42	31.20 31.15
Hornblende, G 107, ex Quartz-diorite (Yeoval, N.S.W., Aust.)	—	—	12.64 12.61
Hornblende, Y 151, ex Quartz-diorite (Yeoval, N.S.W., Aust.)	—	—	9.91 9.95

[a] Limits of Acceptance, Geological Survey Bulletin 1113.
[b] Analysed by C. E. S. Davies.
[c] Analysed by A. J. Easton.
[d] Analysed by Vertie C. Smith[17].

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SUMMARY

Macro-analytical schemes are described for the determination of aluminium, total iron and iron(II), as part of the complete analysis of silicate rocks and minerals. Solvent extraction eliminates interferences before titration of aluminium with DCTA. Iron(III) is extracted with MIBK and determined indirectly with EDTA. Iron(II) is determined by potentiometric titration under an inert atmosphere. Interferences are removed with 2,4-pentanedione and carbon tetrachloride before the determination of calcium and magnesium.

RÉSUMÉ

Des schémas de macroanalyse sont décrits pour le dosage de l'aluminium, du fer total et du fer(II) dans des silicates et autres minerais. Une extraction par solvant élimine les interférences avant titrage de l'aluminium au moyen de DCTA. Le fer(III) est extrait avec MIBK et dosé indirectement au moyen d'EDTA. Le fer(II) est dosé par titrage potentiométrique dans une atmosphère inerte. On élimine des interférences à l'aide de 2,4-pentanedione et tétrachlorure de carbone avant le dosage du calcium et du magnésium.

ZUSAMMENFASSUNG

Für die Bestimmung von Aluminium, Gesamteisen und Eisen(II) als Teil einer vollständigen Analyse von Silicatgesteinen und Mineralien werden makroanalytische Schemata beschrieben. Vor der Titration des Aluminiums mit DCTA werden Störungen durch Flüssigextraktion eliminiert. Eisen(III) wird mit MIBK extrahiert und indirekt mit AEDTE bestimmt. Eisen(II) wird durch potentiometrische Titration unter inerter Atmosphäre bestimmt. Vor der Bestimmung von Calcium und Magnesium werden Störungen mit 2,4-Pentandion und Tetrachlorkohlenstoff beseitigt.

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A CATALYTIC METHOD FOR THE DETERMINATION OF NICKEL

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Catalytic reactions have been used for the determination of traces of a number of metal ions[1]. However, no direct catalytic reaction has been used for the determination of nickel. Although nickel and some of its compounds are efficient catalysts in certain heterogeneous systems, only a few reactions in aqueous solution are known to be catalyzed by nickel ions. Among these are the reactions of permanganate in alkaline solution. For example, STAMM[2] recommended the addition of nickel, cobalt(II) or copper(II) ions to speed up the titration reaction between alkaline permanganate and formate. Likewise, the decomposition of permanganate in alkaline solution is catalyzed by traces of nickel and other ions[3,4]. These reactions offered possibilities for the development of a catalytic method for determining traces of nickel. In this paper, an investigation of the catalysis of the permanganate–formate reaction is described and the development of a method for the determination of nickel based on the decomposition of permanganate in alkaline solution is outlined.

THE FORMATE–PERMANGANATE REACTION

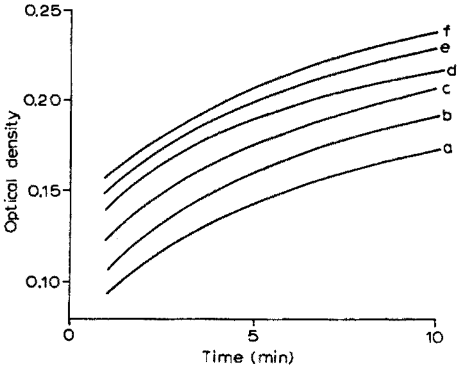
In alkaline solution, formate reduces permanganate to manganate:

$$2\ MnO_4^- + HCOO^- + 3\ OH^- \rightarrow 2\ MnO_4^{2-} + CO_3^{2-} + 2\ H_2O \qquad (1)$$

The reaction can be followed spectrophotometrically at 505 nm (disappearance of permanganate) or 600 nm (appearance of manganate). STAMM[2] prevented reduction of the manganate by precipitating it with barium, but such a procedure would be inconvenient in a spectrophotometric method. When the rate of formation of manganate by the reaction of permanganate with a twenty-fold excess of cyanide, in *ca.* 1 *N* sodium hydroxide solution, was followed spectrophotometrically at 600 nm, it was found that the amount of manganate reached a maximum after 10 min, and was constant for a further 30 min. This demonstrates that any further reaction with the manganate (even when the relatively rapidly oxidised cyanide is used) is very slow under these conditions, and would have no measurable effect on rate measurements based on the formation of manganate. Thus no special precautions to prevent further reaction are necessary.

The effect of nickel ions

The effect of 0–1 p.p.m. of nickel ions on the rate of the formate–permanganate reaction is shown in Fig. 1. The same effect was observed when a permanganate solution 10 times stronger was used. The nickel gives only an *initial* enhancement to the reaction rate. This effect has ceased after less than a minute (when the first spectrophotometric readings are made), which indicates that the initial catalysis is quickly suppressed. It is significant that, when larger nickel concentrations were used, a brown precipitate was formed, containing 13% Mn and 48.5% Ni. A similar precipitate appeared when nickel ions were added to a manganate solution: this precipitate was clearly visible when only 10 p.p.m. of nickel were present. A similar precipitate was observed[5] when nickel was added to a strongly alkaline permanganate solution. The pink permanganate colour was removed, and manganate was produced.



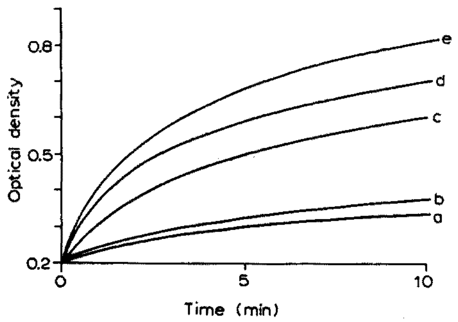


Fig. 1. The reaction of $4.5 \cdot 10^{-4} M$ MnO_4^- with $4.5 \cdot 10^{-4} M$ sodium formate in *ca.* 0.5 N NaOH solution, measured at 600 nm, in the presence of (a) 0, (b) 0.18, (c) 0.36, (d) 0.55, (e) 0.73, (f) 0.91 p.p.m. of Ni^{2+}.

Fig. 2. The decomposition of $7.7 \cdot 10^{-4} M$ MnO_4^- in 0.38 M NaOH solution, $9.2 \cdot 10^{-3} M$ in acetodiphosphonic acid, in the presence of (a) 0, (b) 0.15, (c) 0.62, (d) 0.92, (e) 1.23 p.p.m. of Ni^{2+}, measured at 600 nm.

The optical density differences between the various curves in Fig. 1 are reasonably constant throughout the reaction, and are approximately proportional to the initial nickel concentration. It was possible to calculate, therefore, that for each nickel ion initially present, *ca.* 1.2 more permanganate ions were reduced than would have been reduced in the absence of nickel ions. This indicated that the catalytic activity of the nickel was destroyed after its first catalytic cycle, possibly by forming an insoluble species with the manganate it helped to produce. It was necessary to prevent this precipitation in order to increase the catalytic efficiency of the nickel ions. Such a precipitation is also probably responsible for the rapid deactivation of silver added as a catalyst in the formate–permanganate titration in alkaline solution[5]. This difficulty was overcome by including silver with the titrant so that it was continually replenished.

Four complexing agents were investigated as reagents for preventing the rapid deactivation of the catalytic properties of nickel ions. Of these, dimethylglyoxime, triethylenetetramine, and tartrate were oxidised rapidly, and thus were useless. Only acetodiphosphonic acid* ($H_2O_3P–CCH_3OH–PO_3H_2$) allowed nickel to maintain its catalytic activity for suitably long periods. Moreover, in the presence of this compound,

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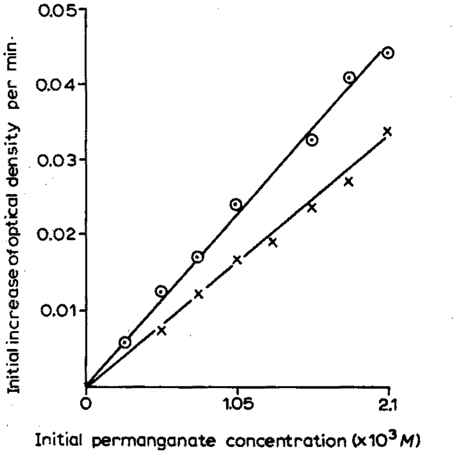
* This is a trivial name for 1-hydroxyethylidene-1,1-diphosphonic acid.

the catalyzed decomposition of permanganate itself in alkaline solution became sufficiently rapid for use in the determination of traces of nickel, so that the addition of formate became unnecessary.

Figure 2 shows the effect of various concentrations of nickel on the rate of the decomposition of permanganate in the presence of acetodiphosphonic acid. Analysis of these curves shows a linear relationship between the reciprocal of the reaction time and the square of the nickel concentration (see Fig. 5).

KINETICS OF THE ALKALINE PERMANGANATE DECOMPOSITION REACTION

The curves in Figs. 2 and 5 show that the reaction is second order with respect to nickel ions. Figure 3 shows the dependence of the initial reaction rate on the initial permanganate concentration, in the presence and in the absence of nickel ions. In both instances the straight line plot indicates that the reaction is first order with respect to permanganate.



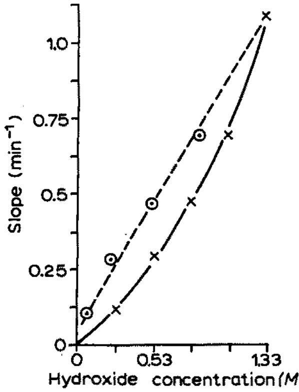


Fig. 3. Variation of initial MnO_4^- decomposition rate with initial MnO_4^- concn. ($2.7 \cdot 10^{-4}$–$2.1 \cdot 10^{-3}M$), in solutions 0.13 M in NaOH, and $3.2 \cdot 10^{-3}M$ in acetodiphosphonic acid, in the presence of (a) 0, (b) 0.133 p.p.m. of Ni^{2+} (600 nm).

Fig. 4. Slopes of log $[MnO_4^-]$ *vs.* time plots, plotted against $[OH^-]$ (×) and $[OH^-]^2$ ⊙.

Tests showed that variation of the acetodiphosphonic acid concentration between 0.0011 and 0.0032 M had no effect on the rate of the uncatalyzed reaction, and that variation between 0.0005 and 0.0032 M had no effect on the reaction catalyzed by 0.13 p.p.m. of nickel, in solutions $6.7 \cdot 10^{-4} M$ in permanganate and 0.44 M in sodium hydroxide. The catalyzed reaction was much slower, however, in the absence of the acetodiphosphonic acid.

Effect of hydroxide

The reactions of solutions $1.33 \cdot 10^{-3}M$ in permanganate and acetodiphosphonic acid, containing 0.133 p.p.m. of nickel ions, when the solutions were 0.27–1.33 M in sodium hydroxide, were followed. Linear plots of log (permanganate concentration) *vs.* time were obtained in the range 1–5 min. Figure 4 gives a plot of the slopes of these lines *vs.* hydroxide concentration and (hydroxide concentration)^2. The plots can be interpreted either to indicate a reaction second order in hydroxide at concentrations greater than 1 M in hydroxide, or a reaction first order in hydroxide at all hydroxide concentrations, with the apparent deviation from first order dependence resulting from an increasing concentration of catalyst present as an impurity in the sodium hydroxide. The probable second order dependence on catalyst concentration adequately accounts for the shape of the plot. The experiments also indicate that the hydroxide concentration must be rigidly controlled if accurate analytical results are to be obtained.

Reaction mechanism

The overall reaction for the decomposition of permanganate in alkaline solution is:

$$4\,MnO_4^- + 4\,OH^- \rightarrow 4\,MnO_4^{2-} + 2\,H_2O + O_2 \tag{2}$$

The detailed mechanism has not been established unequivocally[6] but the reaction sequence given by SYMONS[7] is generally accepted:

$$MnO_4^- + OH^- \overset{k_1}{\rightleftharpoons} MnO_4^{2-} + \cdot OH \tag{3}$$

$$\cdot OH + OH^- \xrightarrow{k_2} \cdot O^-,\ \cdot O_2H,\ \cdot O_2H_2^-\ \text{etc.} \tag{4}$$

Recent investigations[3,8], however, indicate that the kinetic evidence for the mechanism may not be completely reliable because of the unsuspected presence of catalytic ions. LANDSBERG AND THIELE[4] measured the catalytic effect of a number of metal ions, at a concentration of $5 \cdot 10^{-4}$ M, and calculated the consequent increase in k_1 and k_2. The results showed that both reactions were catalyzed by metal ions (Cu^{2+}, Ag^+, Ni^{2+}, Co^{3+}, Pb^{2+}, etc.).

There is general agreement that the uncatalyzed reaction is first order in permanganate, and the most recent studies[3] show that it is also first order in hydroxyl ions. The present study shows that the catalyzed reaction is second order in catalyst, and that the initial reaction rate is given by:

$$\frac{d[MnO_4^{2-}]}{dt} = k[MnO_4^-]_t[Ni^{2+}]^2[OH^-]_t^n \qquad (n = 1 \text{ or } 2)$$

This can be accounted for if the reaction scheme involves the formation of a bi-nuclear μ-hydroxo nickel species:

$$2\,Ni^{2+} + n\,OH^- \rightleftharpoons [Ni(II)_2(OH)_n] \qquad (n = 1 \text{ or } 2) \tag{5}$$

where only the bridging hydroxyl groups are shown. The other co-ordination positions will be occupied by water molecules, hydroxyl ions or acetodiphosphonate ions. There is evidence that all the ions found to catalyze this reaction (except copper) form such polynuclear complexes[9]. The complex would be oxidised by the permanganate *via* the nickel ion:

$$[Ni(II)_2(OH)_n] + MnO_4^- \rightleftharpoons [Ni(II)Ni(III)(OH)_n] + MnO_4^{2-} \tag{6}$$

The stability of the bridged complex would allow sufficient time for the efficient oxidation of the hydroxyl ion by the nickel(III):

$$[\mathrm{Ni(II)Ni(III)(OH)}_n] \rightleftharpoons [\mathrm{Ni(II)_2(OH)}_{n-1}\cdot\mathrm{OH}] \qquad (7)$$

The reaction could then continue:

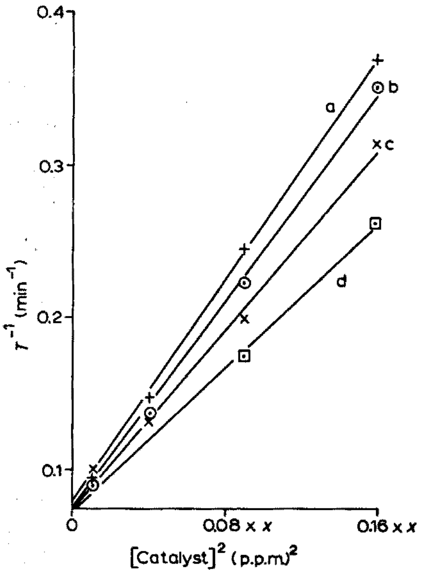
$$[\mathrm{Ni(II)_2(OH)}_{n-1}\cdot\mathrm{OH}] \rightleftharpoons 2\ \mathrm{Ni(II)} + (n-1)\ \mathrm{OH}^- + \cdot\mathrm{OH} \qquad (8a)$$

or $$[\mathrm{Ni(II)_2(OH)}_{n-1}\cdot\mathrm{OH}] + \mathrm{OH}^- \rightleftharpoons [\mathrm{Ni(II)_2(OH)}_n] + \cdot\mathrm{OH} \qquad (8b)$$

The function of the acetodiphosphonic acid has not been established unequivocally. It is possible that it is oxidised to some extent during the reaction. If this reaction were fast compared to the initial decomposition of permanganate, the kinetics would indeed be independent of acetodiphosphonic acid concentration. Nevertheless, the reagent prolongs the catalytic life of nickel ions in this system, which indicates that the reagent must have another function, probably that of a solubilising agent for the catalyst. It could function by preventing the precipitation of basic nickel manganate.

EXPERIMENTAL

All reagents were AR grade, except the sodium hydroxide, hydrochloric acid, ammonia (reagent grade), and acetodiphosphonic acid (Albright and Wilson (Mfg.) Ltd., Oldbury, Birmingham). The same apparatus and conditions were used in establishing the kinetics of the reaction and for the determination of nickel. In order to keep experimental manipulations to a minimum, no further purification of reagents



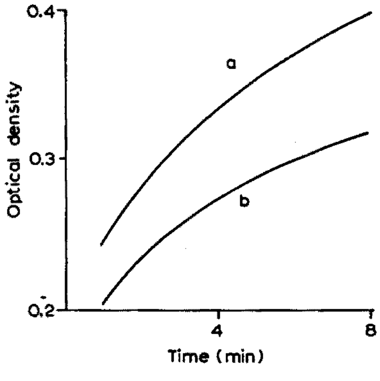


Fig. 5. Plot of T^{-1} *vs.* [catalyst]^2 for the reactions catalyzed by (a) Ag^+, (b) Co^{2+}, (c) Ni^{2+}, (d) Cu^{2+} under the conditions of the analytical procedure. Curve (c) is a typical calibration graph for Ni^{2+}. $x = 1$ for Ni^{2+} and Co^{2+}, 100 for Cu^{2+}, 0.04 for Ag^+.

Fig. 6. A comparison of reaction rates for the reaction catalyzed by 0.28 p.p.m. of Ni^{2+} in solutions (a) 0.0 *M*, (b) 0.035 *M* in PO_4^{3-}.

was made, nor was it found necessary to use a thermostat. Thus, changes in optical density were measured in 1-cm cells in a Unicam SP 600 spectrophotometer, at ambient temperature (20° ± 5°).

Solutions

Water distilled from an all-glass apparatus was used to make up all the solutions. $AgNO_3$, $NiSO_4$, $CuSO_4$ and $Co(NO_3)_2$ were used in making up suitable solutions for analysis.

Sodium hydroxide–acetodiphosphonic acid. Dissolve sodium hydroxide (10 g) and acetodiphosphonic acid (0.25 g) in water and dilute to 100 ml.

Dimethylglyoxime (1%). Dissolve 1 g in the minimum of dilute sodium hydroxide solution, and dilute with water to 100 ml.

Procedure for determining nickel in the absence of interfering ions

Add to 5.00 ml of an approximately neutral nickel solution, containing 0–1.00 p.p.m. of Ni, exactly 2.00 ml of the alkaline acetodiphosphonic acid solution. Then add, with mixing, 0.500 ml of 0.01 *M* permanganate solution. Start a stop-clock half way through the latter addition. Transfer the solution to a spectrophotometric cell, and measure the time (T) required for the optical density to reach 0.300 *vs.* a distilled water blank, at 600 nm.

Carry out the experiment with solutions containing 0.1, 0.2, 0.3 and 0.4 p.p.m. of nickel, and produce a calibration graph by plotting T^{-1} *vs.* $[Ni^{2+}]^2$; a typical graph is shown in Fig. 5. Similar experiments with the "unknowns" should be carried out in succession and their concentrations found from the calibration curve.

Procedure for determining nickel in the presence of interfering ions

Add to 10 ml of the nickel solution (0–0.4 p.p.m.), in a separating funnel, 3 ml of pH 9.15 buffer solution (prepared from a Soloid tablet), 1% dimethylglyoxime solution (1 ml) and sodium citrate (50 mg). Extract with chloroform (2 × 2 ml), wash the combined extracts with 3 *N* ammonia solution (5 ml), and then back-extract with 0.5 *N* hydrochloric acid (10 ml). Evaporate the acidic solution almost to dryness, and wash the residue with water into a 10-ml volumetric flask. Make up to the mark, and analyze a 5-ml aliquot of this solution by the above procedure. Repeat the entire procedure with suitable standard solutions of nickel, and construct a calibration graph as before.

RESULTS

Initial experiments showed that solutions containing more than 0.2 p.p.m. of nickel could be analysed with an accuracy of 3–4%, but that below this concentration the accuracy and precision deteriorated rapidly because of the second-power concentration relationship for the catalyst. For instance, 0.1 p.p.m. could only be determined to ± 10%. Errors for replicate determinations on nickel solutions of known nickel concentrations are summarized in Table I. The determination of "unknown" pure nickel solutions was then carried out. Because of possible long-term changes in the ambient temperature, a calibration curve had to be prepared for each set of unknowns. The results are given in Table II.

TABLE I

PRECISION OF REPLICATE NICKEL DETERMINATIONS

Ni concn. (p.p.m.)	0.1	0.2	0.3	0.4
No. of detns.	8	9	9	9
Mean % error	±7.4	±2.9	±0.8	±0.8

TABLE II

THE ANALYSIS OF "UNKNOWN" PURE NICKEL SOLUTIONS
(Analyses were done in random order at different times)

Ni (p.p.m.)		*Difference*	*Ni (p.p.m.)*		*Difference*	*Ni (p.p.m.)*		*Difference*
Added	*Found*	*(%)*	*Added*	*Found*	*(%)*	*Added*	*Found*	*(%)*
0.120[a]	0.134	10	0.250	0.264	5.6	0.486	0.471	−3.1
0.150	0.141	−6	0.320	0.324	1.3	0.500	0.495	−1.0
0.160	0.169	6	0.390	0.416	6.7	0.520	0.508	−2.3
0.215	0.230	7.0	0.418	0.418	0.0	0.560	0.561	0.2
0.240	0.259	7.9	0.450[b]	0.442	−1.8	0.650[c]	0.652	0.3
0.250	0.244	−2.4	0.476	0.463	1.3			

Reaction times were [a] 735 sec, [b] 200 sec, [c] 105 sec.

The precision with which high concentrations of nickel can be determined is limited by the rapid rate of the reaction, and hence the decreased reaction times. Thus nickel concentrations greater than about 1 p.p.m. would be determined with decreased precision, using the conditions outlined above. Variation of these conditions, however, should allow this range to be extended. Very small nickel concentrations (<0.1 p.p.m.), on the other hand, only slightly enhance the reaction rate, so that variations in the rate of the uncatalyzed reaction become significant sources of error. The slow reaction also makes it difficult to establish when the required optical density is reached.

Interferences

Cations. The following metal ions were added (in 0.5-mg amounts) to the reaction solution in place of the nickel: Ag, Au(III), Bi(III), Cd, Ce(IV), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Hf, In, Ir(IV), La, Mn(II), Mo(VI), Na, Nb, Os(VIII), Pb, Pd, Pt, Re(IV), Rh, Ru(IV), Sn(IV), Sr, Ta, Th, Ti(IV), U(VI), V(V), V(III), Zr. The only species that substantially catalyzed the reaction at the p.p.m. level, and would thus interfere when present in trace amounts, were Ag^+, Co^{2+} and Cu^{2+}. Iridium had some activity, and rhodium and iron(III) were about one-thousandth as effective as nickel. Iron(II) and chromium(III) did not catalyze the reaction, but were oxidised by the permanganate, and thus interfered when present in p.p.m. concentrations. Cerium(IV) precipitated in the alkaline solution, and thus interfered with the spectrophotometric measurement. The other ions neither had a catalytic effect, nor interfered with the determination in any other way.

A more detailed investigation of the catalysis by silver, cobalt and copper was made, using the same procedure as for the determination of nickel; the solutions contained one-fifth, the same, and 10 times the concentration of metal ion, respectively, as that of nickel. The T^{-1} *vs.* [metal ion]^2 plots are in Fig. 5. All give excellent straight lines, showing that the catalytic mechanism is probably the same in all instances, and involves two metal ions. The relative molar quantities of metal ions having an equivalent catalytic effect are

Ag^+(1.0); Co^{2+}(8.8); Ni^{2+}(9.0); Cu^{2+}(101)

This compares with Cu^{2+} (0.73); Ag^+ (1.0); Pb^{2+} (2.3); Ni^{2+}, Co^{3+} (2.4); Fe^{3+} (3.6) for the overall catalysis calculated from the results of LANDSBERG AND THIELE[4] who used unpurified reagents, and can also be compared with the order of catalytic efficiency obtained by VEPŘEK-ŠIŠKA *et al.*[3], who used highly purified reagents:

$Ni^{2+} > Co^{3+} > Fe^{3+}$, Ag^+, Cu^{2+}, Pb^{2+}.

The complexing effect of the acetodiphosphonic acid probably accounts for the difference between the order of catalytic efficiency found in the present investigation and that found by the previous workers[3,4], whereas the presence of catalytic impurities may account for the discrepancies between the earlier workers.

It was established that the catalytic effects of cobalt and nickel, copper and nickel, and copper and cobalt are additive.

Anions: Fluoride, nitrate, chloride and sulphate were without effect. Phosphate (added as $NH_4H_2PO_4$), however, considerably reduced the reaction rate (Fig. 6). Oxalate (0.006–0.04 M) had no effect on the uncatalyzed reaction, but the catalysis by nickel was considerably suppressed. The initial reaction rate in such circumstances was approximately inversely proportional to the oxalate concentration, and there is little doubt that the addition of sufficient oxalate would suppress the catalysis completely.

Organic compounds: Most organic compounds interfered because they were readily oxidised.

Elimination of metal ion interferences

A solvent extraction procedure was applied selectively to remove nickel from solutions containing various interfering cations. Nickel dimethylglyoximate was extracted into chloroform, and the nickel back-extracted into 0.5 N hydrochloric acid. However, sufficient chloroform was dissolved in this aqueous solution to react appreciably with the permanganate, and thus vitiate a nickel determination. Evaporation to near dryness sufficed to reduce the chloroform concentration below its interference level, so that the residual material could simply be dissolved in water, and then analysed by the original procedure. When this process was applied to pure nickel solutions, the results obtained compared favourably with those obtained by the non-extraction procedure. Results obtained when interfering cations were present are given in Table III. They show that the procedure prevents the interference of these metal ions in concentrations up to 100 p.p.m. If they are present in larger concentrations, it may be necessary to take additional precautions to avoid their extraction or interference, such as those suggested by NIELSCH[10] and KAWASE[11].

Extraction of more dilute ($>$0.02 p.p.m.) nickel solutions

The extraction procedure was used to increase smaller concentrations (0.02–

TABLE III

DETERMINATION OF 0.500 p.p.m. OF NICKEL IN THE PRESENCE OF INTERFERING IONS

Other ions[a] *present*	*Ni found (p.p.m.)*	*Error (%)*	*Other ions*[a] *present*	*Ni found (p.p.m.)*	*Error (%)*
Co^{2+}	0.508	1.6	Ag^+, Cu^{2+}	0.492	−1.6
	0.492	−1.6	Ag^+, Co^{2+}	0.478	−6.5
	0.492	−1.6	Fe^{3+}	0.492	−1.6
Cu^{2+}	0.492	−1.6	Fe^{3+}, Co^{3+}	0.508	1.6
Cu^{2+}, Co^{2+}	0.508	1.6	Fe^{3+}, Au^{3+}	0.508	1.6
Ag^+	0.478	−6.5	Fe^{3+}, Cu^{2+}	0.492	−1.6

[a] 1 mg of each ion.

TABLE IV

REPLICATE DETERMINATIONS OF 0.025 p.p.m. OF NICKEL

					Mean
Ni found (p.p.m.)	0.0276	0.0249	0.0279	0.0243	0.0262
Error (%)	10	0	12	−3	5

0.08 p.p.m.) of nickel, and thus extend the range of the method. The quality of the results was poorer, and it was not possible to improve on them by variations in the extraction procedure, or by taking precautions to reduce the amount of unwanted material reaching the final solution. The reproducibility of replicate determinations of 0.025 p.p.m. of nickel in 100 ml of solution is given in Table IV. Down to 0.02 p.p.m. of nickel can be determined by this method with some loss of precision, and an increased incidence of spurious results.

CONCLUSION

The catalytic effect of nickel on the decomposition of permanganate in alkaline solution, in the presence of acetodiphosphonic acid gives a precise and rapid means of determining 0.25–0.65 p.p.m. of nickel, and a progressively less precise means for smaller concentrations, in the presence of many metal ions. The method is as sensitive as the most sensitive spectrophotometric methods for nickel[12]. Little additional apparatus (a stop-clock) is required, and there is no need to purify the reagents before use. Furthermore, the method can easily be automated. If special attention were given to the removal of the traces of metal ions present in the reagents, the sensitivity of the procedure could probably be increased a hundred-fold, in accordance with the findings of VEPŘEK-ŠIŠKA *et al.*[3]. It is also likely that the reaction would be useful for the determination of silver and cobalt, the former down to 10^{-2} p.p.m., and cobalt in a similar concentration to that of nickel.

We are grateful to Professor R. BELCHER for his interest and encouragement, and to Albright and Wilson (Mfg.) Co., Ltd., Oldbury, for providing the sample of acetodiphosphonic acid. D. M. thanks the Department of Chemistry for a maintenance grant.

SUMMARY

The catalytic effect of nickel on the decomposition of permanganate in alkaline solution in the presence of acetodiphosphonic acid is used as a basis for a method for the determination of 0.1–0.7 p.p.m. of nickel. A solvent extraction procedure eliminates the interferences of silver, cobalt, copper and iron, and can be used to concentrate lower concentrations of nickel.

RÉSUMÉ

Une méthode catalytique est proposée pour le dosage du nickel; elle est basée sur l'effet catalytique du nickel sur la décomposition d'une solution alcaline de permanganate, en présence d'acide acétodiphosphonique. Quantités dosables par ce procédé: 0.1–0.7 p.p.m. de nickel. Une extraction dans un solvant permet d'éliminer argent, cobalt, cuivre et fer; elle permet aussi de concentrer des teneurs trop faibles de nickel.

ZUSAMMENFASSUNG

Der katalytische Effekt von Nickel auf die Zersetzung von Permanganat in alkalischer Lösung in Gegenwart von Acetodiphosphorsäure wird als Grundlage für eine Methode zur Bestimmung von 0.1–0.7 p.p.m. Nickel verwendet. Durch Flüssigextraktion werden Störungen durch Silber, Cobalt, Kupfer und Eisen eliminiert und gleichzeitig eine Anreicherung geringer Konzentrationen Nickel erreicht.

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UTILISATION DE L'ULTRACENTRIFUGEUSE POUR LA MESURE DES MASSES ET POUR L'ETUDE DE LA POLYDISPERSITE DES POLYMERES DE SYNTHESE*

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(Reçu le 2 avril, 1967)

L'ultracentrifugation a été et est encore une des techniques de base de la biochimie[1-4] et il n'existe pratiquement pas de laboratoire travaillant dans ce domaine qui ne possède une ultracentrifugeuse. Par contre, l'application de cette technique aux polymères de synthèse s'est développée beaucoup plus lentement et bien que beaucoup de laboratoires possédent l'équipement nécessaire pour effectuer de telles mesures, on ne peut pas dire que l'apport de l'ultracentrifugation à la caractérisation des polymères synthétiques soit considérable. Pourtant, au cours des dernières années, un certain nombre de nouveaux procédés ont été mis au point par les biologistes; ils peuvent s'appliquer aux polymères de synthèse et offrent de nouvelles possibilités d'analyse que nous tâcherons de résumer brièvement.

Les mesures par ultracentrifugation se classent en 2 groupes distincts, les mesures cinétiques dans lesquelles on étudie l'évolution au cours du temps d'une solution soumise à un champ de force et les mesures d'équilibre dans lesquelles on étudie la répartition des molécules dans la solution quand l'équilibre est atteint.

Ces 2 techniques permettent de mesurer la masse moléculaire des polymères ainsi que leur polydispersité qui sont les paramètres de base servant à la caractérisation d'un échantillon. On peut aussi, du moins en principe, obtenir par ultracentrifugation des informations sur la thermodynamique des solutions, et déterminer par cette méthode des quantités comme le second coefficient de viriel; il semble cependant qu'il s'agisse là de méthodes assez détournées, plus difficiles à mettre en oeuvre que les méthodes classiques, aussi les applications de cette technique à ce type de problèmes sont assez rares.

Dans les mesures cinétiques, on mesure les phénomènes de transport, c'est-à-dire des phénomènes liés à la morphologie des molécules, qui permettent de déterminer des grandeurs telles que le coefficient de frottement. On peut donc espérer utiliser cette technique pour mesurer les dimensions moléculaires et caractériser par exemple le degré de branchement de molécules.

Enfin, le volume spécifique joue dans toutes ces expériences un rôle important, car c'est grâce à la différence entre celui du solvant et celui du polymère que l'on observe les phénomènes de sédimentation. On peut donc, grâce à cette technique, mesurer dans les mélanges de solvant l'adsorption préférentielle. Aussi, cette technique a-t-elle été utilisée pour étudier ce phénomène. Nous allons donc, dans le cadre de cet exposé, rappeler brièvement un certain nombre de résultats classiques en nous

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* This paper was read at the International Symposium on Physical Methods of Separation in Chemical Analysis, Amsterdam, April 1967.

étendant plus sur les techniques récentes qui semblent devoir renouveler l'intérêt de l'ultracentrifugation dans ce domaine.

MÉTHODES CLASSIQUES D'ULTRACENTRIFUGATION

Nous ne reviendrons pas sur la description de l'appareillage expérimental utilisé. Il est bien connu. Nous appellerons r la distance d'un niveau donné de la cellule à l'axe de rotation. Si ω désigne la vitesse angulaire de rotation, une particule de masse m sera soumise d'une part à une force f_1, telle que $f_1 = m\,\omega^2 x$; si la particule, de volume spécifique partiel $\bar{v}$ est plongée dans un liquide de masse spécifique ϱ, la poussée d'Archimède sera $f_2 = -\,m\,\bar{v}\,\varrho\,\omega^2 r$. La force résultante sera donc

$$F = f_1 + f_2 = m(1-\bar{v}\varrho)\omega^2 r$$

En plus de cette force, la particule est soumise à l'agitation thermique ce qui va entraîner, dès que la concentration n'est plus uniforme, l'apparition de phénomènes de diffusion. Suivant l'importance relative de ces 2 phénomènes, on parlera de mesures de vitesse de sédimentation ou de mesures d'équilibre de sédimentation.

Mesures de vitesse de sédimentation

Rappel théorique et domaines d'application. Dans ce cas, c'est l'effet de la force F qui l'emporte sur les effets de la diffusion. Sous l'influence de cette force, la particule va prendre une vitesse $\mathrm{d}r/\mathrm{d}t$ telle que

$$m(1-\bar{v}\varrho)\omega^2 r = f\,\mathrm{d}r/\mathrm{d}t$$

où f représente le coefficient de frottement de la particule sur le solvant. La quantité $m\,(1-\bar{v}\varrho)/f$ ne dépend que du système particule–solvant. On définit la constante de sédimentation s par la relation

$$s = \frac{m(1-\varrho\bar{v})}{f} = \frac{1}{\omega^2 r}\,\frac{\mathrm{d}r}{\mathrm{d}t}$$

Ce qui conduit à l'équation bien connue de Svedberg

$$s = M(1-\bar{v}\varrho)/f\mathcal{N}$$

$\mathcal{N}$ = nombre d'Avogadro
M = masse moléculaire du polymère

C'est cette relation qui est la base de l'utilisation de l'ultracentrifugeuse. En effet, toutes les molécules se déplaçant avec la même vitesse, il apparaît rapidement du solvant pur au haut de la cellule. On peut donc suivre en fonction du temps, le déplacement de la frontière solvant–solution, ce qui permet le calcul de s. Il ne faut pas oublier que cette facon de procéder constitue une approximation. En effet, la forme de la frontière solvant–solution dépend du coefficient de diffusion de translation du soluté. La répartition exacte des concentrations dans la cellule en fonction du temps a été calculée par FAXEN[5].

La mesure de s par cette méthode n'est utilisable que s'il se forme dans la cellule de mesure une frontière solvant–solution, c'est-à-dire uniquement si la migration des macromolécules due au champ de force centrifuge est importante devant les mouvements browniens. Il faut donc que la vitesse de rotation ω soit assez grande et que la masse moléculaire M du soluté soit suffisamment élevée. Comme la vitesse dépend également de la quantité $1 - \bar{v}\varrho$, il faut que les masses spécifiques des particules et du solvant soient aussi différentes que possible (signalons que si $1 - \bar{v}\varrho < 0$, on aura une flottation qui permet aussi de mesurer s). En pratique, les mesures de vitesse de sédimentation sont possibles pour des valeurs raisonnables de $1 - \bar{v}\varrho$ et jusqu'à une limite inférieure de M qui est de l'ordre de 15,000 à 20,000.

Facteurs correctifs. Avant d'étudier les résultats que fournit cette méthode, il est important de citer les facteurs correctifs dont il faut tenir compte dans ce type de mesures, si l'on veut arriver à des résultats quantitatifs exacts.

(*1*) Au fur et à mesure que les macromolécules se déplacent vers le fond de la cellule, elles se trouvent dans un milieu de plus en plus dilué: ceci est dû à la forme en secteur circulaire de la cellule. Si s dépend fortement de la concentration, cet effet aura une influence non négligeable sur les valeurs mesurées. Différentes méthodes ont été proposées pour en tenir compte[6–8].

(*2*) Compression du milieu. Les vitesses élevées qui sont généralement utilisées entraînent une valeur importante de l'accélération dans la cellule (de l'ordre de 200,000 g). Dans ces conditions, le milieu est fortement comprimé et les valeurs de ϱ, $\bar{v}$ et de la viscosité du solvant η, varient avec la distance au centre de rotation. Plusieurs auteurs[9–11] ont proposé des méthodes qui permettent d'éliminer cet inconvénient qui est plus important dans les solvants organiques que dans l'eau.

(*3*) Influence de la concentration. Les valeurs de s mesurées vont dépendre en général de la concentration c en polymère. Il faudra donc extrapoler les valeurs de s obtenues pour plusieurs valeurs de c à dilution infinie[12,13]. Dans le cas d'un mélange de polymères dans lequel la variation de s avec c est très différente d'une espèce à l'autre, il peut apparaître un artefact[14]. Cette obligation d'extrapoler à concentration nulle est une des difficultés majeures de l'utilisation de l'ultracentrifugation. Les variations de s avec c dépendant à la fois des interactions thermodynamiques et hydrodynamiques entre molécules, il n'est en principe pas possible de les éliminer en travaillant en solvant θ, c'est-à-dire dans un solvant pour lequel la pression osmotique est proportionnelle à la concentration dans un assez large domaine de concentration. Pourtant, il semble qu'en opérant dans ces conditions, les interactions deviennent très faibles et que l'extrapolation soit beaucoup plus facile.

Résultats

Masse moléculaire. Comme nous venons de le voir, et après un certain nombre de corrections, il est possible dans le cas d'un corps pur, de calculer la valeur de M à partir de s grâce à la relation de Svedberg. Il faut connaître pour cela, la valeur de $(1 - \bar{v}\varrho)$ et de f. On obtient f par des mesures de diffusion de translation. On sait, en effet, que le coefficient D est lié au coefficient de frottement f par la relation $D = KT/f$ où K est la constante des gaz parfaits et T la température absolue. Nous désignerons la valeur de M déterminée ainsi par $M_{\mathrm{s,D}}$[13].

On peut effectuer le même calcul si l'échantillon est polydispersé. La valeur de $M_{\mathrm{s,D}}$ obtenue est alors une valeur moyenne, non définissable mathématiquement, des différentes valeurs de M.

On peut également utiliser une relation du type $s = KM^{\alpha}$, en déterminant les valeurs de K et de α à partir d'une série de valeurs de s obtenues avec des fractions de masses connues, d'un échantillon de polymère. La relation est alors applicable à d'autres échantillons de polymère de la même espèce chimique.

Les valeurs des coefficients K et α peuvent être reliées à la forme des macromolécules. Différents calculs ont été proposés, basés sur les propriétés hydrodynamiques et thermodynamiques en solution. Les formules établies s'appliquent aux molécules en chaîne statistique flexible et aux particules rigides[15-19]. Dans des travaux plus récents, on a étudié les cylindres plus ou moins flexibles en utilisant le modèle de la chaîne à longueur de persistance (worm like chain)[20-22].

Ici encore, la valeur de M obtenue, quand les systèmes sont polydisperses, sera une valeur moyenne mal définie.

Polydispersité

L'étude de la vitesse de sédimentation est particulièrement intéressante car elle permet dans certains cas de déterminer non seulement une valeur moyenne de M, mais la courbe de répartition des masses moléculaires de l'échantillon. Pour cela, il faut d'abord déterminer la courbe de répartition des coefficients de sédimentation. Cette répartition est représentée par une fonction $g(s)$ telle que la concentration en poids des molécules dont la constante de sédimentation est comprise entre s et $s+ds$ est donnée par

$$dc = g\ (s)\ ds.$$

La fonction $g(s)$ peut être calculée à partir de la forme de la frontière solvant–solution. En effet, celle-ci dépend de la polydispersité d'une part, de la diffusion de translation des macromolécules d'autre part. Après avoir extrapolé les résultats expérimentaux, à dilution infinie et éliminé l'élargissement de la courbe dû à la diffusion de translation, on peut obtenir $g(s)$[23-25]. Or la quantité intéressante est la distribution des masses moléculaires qui est définie par une fonction $f(M)$ telle que la concentration en poids des molécules dont la masse moléculaire est comprise entre M et $M+dM$ soit donnée par la formule $dc=f(M)dM$. A partir de la fonction $g(s)$ on peut alors calculer $f(M)$. Pour cela, on peut procéder de 2 facons: soit que l'on établisse une relation du type $s=KM^{\alpha}$ qui fournit une valeur de M pour chaque valeur de s[26], soit que l'on détermine par ailleurs la distribution des coefficients de diffusion $h(D)$ de l'échantillon, ce qui permet en combinant $h(D)$ et $g(s)$ d'obtenir $f(M)$[27]. De nombreux travaux ont été consacrés à ce type d'étude, car la courbe de polydispersité est évidemment une donnée importante qui intéresse beaucoup les chimistes et qu'on ne pouvait obtenir en une expérience que par cette technique avant l'apparition de la chromatographie sur gel en phase liquide. A titre d'exemple, HENDERSON *et al.*[28] montrent des résultats obtenus sur un copolymère styrène–butadiène qui indiquent clairement la présence d'un constituant de poids moléculaire élevé.

De même, KALFUS ET MITUS[29] essayent d'obtenir pour une série homologue de polymères des méthodes de routine qui permettent d'éliminer les difficultés d'extrapolation à concentration nulle.

Alors que ce type d'étude est courant dans le domaine de la biologie, son succès n'a été que tout relatif dans le domaine des polymères de synthèse. En effet, dans la plupart des cas, les échantillons bruts de polymérisation correspondent à une distribution à un pic, et ce qui est important, ce sont les "queues" de courbe, c'est-à-dire les faibles pourcentages de masses élevées et de petites masses. Or, vu la précision des méthodes optiques, il est très difficile de déterminer le moment exact où la courbe expérimentale se sépare de la ligne de base, ce qui limite considérablement la précision. Dans tous les cas où il y a des espèces assez différentes pour que les pics soient séparés, cette méthode est très intéressante. Si l'on veut avoir une idée générale de la courbe de distribution la méthode est très utile mais sa précision est limitée et la détermination de faibles quantités d'hétérogénéités est souvent pratiquement impossible.

Enfin, signalons que la vitesse de sédimentation peut aussi être utilisée pour mettre en évidence les interactions des macromolécules avec le solvant[30-32].

Mesures d'équilibre de sédimentation

Pour faire une expérience d'équilibre de sédimentation, on choisit la vitesse de rotation du rotor de façon telle que, compte tenu de la masse moléculaire de l'échantillon étudié, le flux de particules dû à leur sédimentation soit égal au flux de particules inverse dû à l'agitation thermique. Au bout d'un certain temps, on obtient un état d'équilibre qui va se traduire par une répartition caractéristique des concentrations dans la cellule. Il est possible d'appliquer dans ce cas les relations classiques de la thermodynamique, ce qui va se traduire par des résultats mieux définis mathématiquement que lors des mesures de vitesse. Ceci est vrai en particulier en ce qui concerne les moyennes des masses moléculaires.

Rappel théorique et domaines d'application. La théorie complète et rigoureuse de l'équilibre de sédimentation a été faite[2,33]. Nous nous bornerons à indiquer la relation permettant de calculer la masse moléculaire d'un corps pur en solution idéale:

$$\frac{M(1-\bar{v}\varrho)}{2RT}\omega^2\,(r_b{}^2-r_a{}^2)=\frac{c(r_b)-c(r_a)}{c_0}$$

Dans cette équation, R représente la constante des gaz parfaits, c_0 la concentration initiale en polymère, $c(r_b)$ et $c(r_a)$ désignent respectivement la concentration de polymère au fond et au haut de la cellule de centrifugation.

En principe, cette technique est applicable à n'importe quelle solution. En ce qui concerne les solutions macromoléculaires cette application est limitée pour des raisons pratiques. En effet, nous l'avons déjà vu, il faut que le flux dû à la diffusion soit égal à celui de sédimentation. Or, si les particules en solution ont une valeur de s élevée, il faut choisir des vitesses de rotation faibles pour que cette condition soit remplie. Comme cette réduction de la vitesse est limitée inférieurement à une valeur qui est de l'ordre de 2000 tours/min pour les machines classiques, on ne pourra pas étudier des macromolécules dont la masse moléculaire dépasse un certain seuil. Suivant les cas, c'est-à-dire suivant la valeur du facteur $(1-\bar{v}\varrho)$ ce seuil se situe aux environs d'une valeur de M de l'ordre de $2\cdot10^5$ à $5\cdot10^5$.

Le temps nécessaire pour atteindre la répartition d'équilibre du polymère est généralement long. On peut diminuer la durée des expériences, soit en diminuant la hauteur de remplissage de la cellule, soit en partant d'une répartition des concentrations dans la cellule qui se rapproche déjà du gradient que l'on veut obtenir[34], soit en faisant la mesure avant l'obtention de l'équilibre, durant la période transitoire. Cette dernière facon de procéder constitue la méthode d'ARCHIBALD[35,36].

Corrections. Comme pour les mesures de vitesse, la compression de la solution va intervenir. Elle va modifier les valeurs de ϱ et de $\bar{v}$. Le plus souvent, on néglige l'influence de la compression, étant donné les valeurs de la vitesse relativement faibles que l'on utilise.

Si la solution étudiée n'est pas une solution idéale, les résultats obtenus vont dépendre de la concentration c. Les relations mathématiques qui tiennent compte de cet effet ont été établies[37]. La masse moléculaire mesurée est alors une masse "apparente" et il faut extrapoler à dilution infinie selon une loi connue pour obtenir la valeur vraie de M.

Résultats. Comme nous venons de le voir, le calcul de la masse moléculaire d'un corps pur est immédiat.

Si l'échantillon est polydisperse, on exploite les résultats expérimentaux de la même manière et on montre que la valeur de M ainsi obtenue est la valeur moyenne en poids M_w, de toutes les masses moléculaires. L'allure de la courbe expérimentale (en particulier les valeurs de la dérivée aux abscisses r_a et r_b) permet aussi le calcul de la moyenne classique M_z de ces mêmes masses.

Bien que plus longues et plus délicates à mettre en oeuvre que les mesures de vitesse, les mesures d'équilibre peuvent donc être intéressantes dans le cas où l'on veut connaître des valeurs moyennes de M bien définies mathématiquement. Ces mesures ont été rendues plus simples par quelques perfectionnements récents: l'emploi de remplissages très faibles de la cellule (moins de 1 mm de haut); la mise au point d'une optique interférométrique sur les ultracentrifugeuses qui permet de travailler à des concentrations de polymère plus faibles.

Les applications les plus intéressantes de cette technique aux macromolécules se situent dans le domaine des masses moléculaires faibles (1,000 à 200,000).

Une difficulté importante, cependant, rend ces expériences délicates pour des systèmes relativement polydisperses. Il faut, en effet, pour que les mesures soient commodes, ajuster la vitesse de rotation en fonction de la masse moléculaire. Si l'échantillon est très polydisperse, en tournant à une vitesse correspondant à la valeur moyenne, on tournera trop vite pour les grosses masses qui resteront au fond de la cellule et trop lentement pour les petites masses qui resteront en concentration uniforme. Il faudra donc effectuer des expériences à des vitesses différentes, ce qui complique considérablement la situation.

MÉTHODES RÉCENTES D'ULTRACENTRIFUGATION

Caractéristiques générales

Jusqu'à présent, nous n'avons envisagé que le cas des solutions binaires composées d'un solvant et d'un soluté macromoléculaire. Nous appellerons mélange ternaire, une solution composée d'un solvant 1, d'un soluté 2 non macromoléculaire (sel, solvant organique, sucre . . .) et d'un soluté macromoléculaire 3.

La présence du soluté 2 va modifier les phénomènes observés. On pourra toujours faire des mesures de vitesse ou d'équilibre de sédimentation mais il faudra tenir compte du changement des paramètres caractérisant le milieu dans lequel les macromolécules se déplacent: il s'agit de la viscosité η et de la masse spécifique ϱ.

Mais les paramètres caractérisant le polymère peuvent changer également. Si les macromolécules s'entourent préférentiellement de solvant 1 ou de soluté 2, il faudra considérer la particule "solvatée" dans son ensemble. Il faudra donc utiliser un volume spécifique partiel "solvaté" $\bar{v}_s$ et une masse moléculaire "solvatée" M_s. De plus, les macromolécules peuvent changer de forme et de ce fait le coefficient de frottement f va être modifié.

Des expériences de ce genre avec toutes les corrections nécessaires ont été décrites[38,39]. Il semble donc que la présence du soluté 2, ne soit qu'une source de complications expérimentales. Mais l'étude des solutions ternaires a été à l'origine de développements importants de l'ultracentrifugation et de techniques nouvelles dans ce domaine que nous allons passer en revue maintenant.

Equilibre de sédimentation en gradient de densité (E.S.G.D.)

On va utiliser un solvant 1 et un soluté 2 de masses spécifiques (que l'on confond souvent avec les densités) bien différentes. Dans ce mélange, on dissout également du polymère dont nous désignerons maintenant la concentration par c_3. Au démarrage de la centrifugeuse, la cellule de mesure contient donc ce mélange homogène à tous les niveaux. Au bout d'un certain temps, le soluté 2 va être réparti dans la cellule selon une distribution qui répond à celle que nous avons décrite dans le cas de l'équilibre de sédimentation. Si ce soluté 2 est plus dense que le solvant 1, on en trouvera davantage près du fond de la cellule et moins près du haut. Sa concentration au milieu de la cellule sera voisine de sa concentration initiale. Etant donné la différence de masses spécifiques entre 1 et 2, cette répartition de concentration du soluté 2 va se traduire par une répartition continue de masses spécifiques du mélange 1–2 que l'on appelle généralement le "gradient de densité".

Nous allons voir maintenant quel va être le comportement des macromolécules au sein de ce gradient. L'établissement du gradient et la migration des macromolécules se font simultanément au cours de l'expérience. Mais, comme l'état final va être un état d'équilibre, on peut également, pour des raisons de simplification, admettre que ce polymère ne migrera qu'une fois le gradient établi.

Si les proportions du mélange 1–2 ont été choisies de façon telle que la valeur de la masse spécifique du polymère solvaté, $\varrho_s = 1/\bar{v}_s$, soit contenue dans les valeurs de la densité realisées dans la cellule on aura à cet endroit $1-\bar{v}_s\varrho = 0$ pour toutes les macromolécules. Il n'y a donc aucune force de sédimentation qui s'exerce à ce niveau au macromolécules. Nous appellerons r_0 l'abscisse de ce niveau. Les particules situées plus près de l'axe de rotation se trouvent dans le milieu où ϱ est plus faible. Donc $1-\bar{v}\varrho > 0$.

Elles vont sédimenter jusqu'en r_0. De même celles qui se trouvent près du fond de la cellule sont plongées dans un mélange de densité ϱ plus élevée qu'en r_0. Elles vont flotter jusqu'en r_0. Toutes les macromolécules vont donc se rassembler en une bande située en r_0. La largeur de cette bande dépendra de la masse moléculaire du polymère. On montre très simplement que si l'échantillon de polymère n'est pas polydispersé, la répartition de concentration c_3 du polymère est gaussienne autour de r_0, et l'écart-type σ de cette répartition est proportionnel à $M_s^{-1/2}$.

Cette technique qui a été décrite pour la première fois par MESELSON *et al.*[40] a connu un développement considérable comme méthode de recherche en biochimie. Elle a été appliquée plus rarement aux polymères de synthèse[41,42], et aux copolymères[43,44]. Ses conditions d'application sont les suivantes:

Il faut d'abord trouver un mélange 1–2, tel que le gradient de densité obtenu soit assez important et que la valeur de ϱ_s soit contenue dans ce gradient: il faut donc que le polymère soit soluble et les composants 1–2 miscibles dans les conditions requises[45]. Il faut que la masse moléculaire du polymère solvaté soit assez élevée pour que la bande obtenue ne soit pas trop large, et surtout ne dépasse pas les dimensions de la cellule: cette condition est remplie pour des masses moléculaires de l'ordre de 300,000 et au-delà.

Corrections. Dans cette méthode, le rôle des facteurs correctifs est considérable, à la fois en ce qui concerne leur valeur numérique et en ce qui concerne le temps nécessaire à leur détermination.

(*1*) La compression du milieu va intervenir sur plusieurs paramètres et cela différemment suivant le niveau dans la cellule. Elle va modifier à la fois la valeur du gradient de densité qui peut être calculé à partir de la répartition de 2 dans 1. Il s'y superposera un gradient dû à la compression. Elle va modifier également les volumes spécifiques partiels solvatés des macromolécules. On montre qu'il est possible de calculer l'importance de cet effet, en mesurant par ailleurs la différence de compressibilité entre le polymère solvaté et le solvant[46]. On peut aussi faire plusieurs expériences d'E.S.G.D. en utilisant des hauteurs de remplissage différentes de la cellule, et extrapoler les résultats à pression atmosphérique[47].

(*2*) Les macromolécules rassemblées dans une bande, vont se trouver dans un mélange 1–2 de composition différente suivant l'abscisse à laquelle elles se trouvent (plus riche en 2 du côté du fond de la cellule, moins riche en 2 du côté du haut). Comme leur solvatation préférentielle dépend de la composition du mélange 1–2, celle-ci va varier. Ceci introduit une disymétrie dans la répartition de c_3. Pour pouvoir la corriger, il faut connaître la loi de variation de la solvatation avec la composition du mélange 1–2. Ceci peut se faire par différentes méthodes[46,47].

(*3*) A moins d'un hasard, qui ferait que le mélange 1–2 dans les proportions requises soit un solvant θ pour le polymère, la solution ne peut jamais être considérée comme idéale. Les résultats obtenus dépendent de la concentration du polymère. Il faudra donc les extrapoler à dilution infinie: cette extrapolation peut se faire sur les valeurs de M calculées à partir de σ[48]. On pourrait également extrapoler l'ensemble de la courbe de répartition de c_3, point par point, en utilisant une relation telle que l'ont proposée DAYANTIS ET BENOÎT[49]. Ceci n'a pas encore été fait, à notre connaissance.

Résultats. Si l'échantillon n'est pas polydispersé, on peut tirer la valeur de la masse M de la largeur de la distribution de c_3. Nous avons déjà parlé de ce cas. Si l'échantillon est polydispersé, chaque fraction de polymère dont la masse est comprise entre M et $M + \mathrm{d}M$ va former une bande à l'abscisse r_0. Toutes ces bandes seront gaussiennes. La distribution de tout le polymère sera la somme de toutes ces distributions particulières et ne sera plus gaussienne. Sa représentation graphique sera toujours symétrique et présentera toujours 2 points d'inflexion. On peut alors procéder comme on le ferait pour une courbe de Gauss, en appelant σ la distance entre les points d'inflexion. Nous appellerons M_σ la valeur de la masse calculée à partir de σ ainsi définie. On peut montrer que M_σ n'est pas une moyenne classique mais qu'elle est toujours inférieure à la moyenne $M_{5/2}$[42]. Il a été démontré aussi que l'on pouvait, à partir des différents moments de la courbe expérimentale, calculer les moyennes classiques M_n et M_w. C'est ce qu'ont fait HERMANS ET ENDE[41]. Ils obtiennent d'abord des valeurs moyennes, "apparentes", qu'ils extrapolent à dilution infinie pour avoir les valeurs correctes.

C'est certainement dans ce domaine que l'on peut attendre les résultats les plus intéressants en ce qui concerne les mesures d'E.S.G.D. Un échantillon de copolymère présente une double polydispersité: une polydispersité des masses moléculaires et une polydispersité de composition chimique: si les macromolécules sont formées d'enchaînements de monomères A et B, le rapport A/B sera différent d'une molécule à l'autre. Les volumes spécifiques partiels solvatés seront différents et cela pour 2 raisons: d'abord parce que les volumes spécifiques partiels des monomères A et B sont différents et que la valeur de $\bar{v}$ du copolymère dépendra du rapport A/B; ensuite, parce que les 2 sortes de monomères vont se solvater différemment. Cette différence de solvatation préférentielle va encore augmenter la polydispersité des volumes spécifiques partiels solvatés. Si nous considérons toutes les macromolécules ayant une masse M et une composition chimique données, celles-ci vont se rassembler en une distribution gaussienne dans le gradient de densité. C'est le cas d'un corps pur. Si nous ajoutons toutes les autres molécules de même composition mais de masses moléculaires différentes, la répartition des concentrations devient la somme de toutes les distributions gaussiennes centrées sur la même abscisse: c'est le cas que nous avons vu pour les homopolymères polydispersés. Mais les molécules de polymère de composition chimique différente vont donner lieu aux mêmes phénomènes à d'autres abscisses correspondant à d'autres densités.

Finalement, la distribution de tout le polymère dans la cellule consiste en la somme d'un grand nombre de distributions gaussiennes placées les unes à côté des autres et superposées les unes aux autres.

La largeur de cette distribution est donc due à la fois à la valeur des masses moléculaires et à l'importance des fluctuations de composition.

Le grand intérêt de l'E.S.G.D. appliqué aux copolymères est de fournir des renseignements sur ces variations de composition.

Le cas le plus simple est celui où on étudie un mélange de plusieurs composants bien différents. Ce genre d'études a été fait sur des mélanges de copolymères et d'homopolymères. On peut séparer très nettement les 2 espèces et étudier ainsi la pureté d'un échantillon de copolymère[50].

Si la répartition du copolymère est symétrique, on peut avoir une estimation de la polydispersité de composition en admettant que la distance entre les 2 points d'inflexion σ est la somme de 2 facteurs: un terme σ_M calculé à partir de la masse moléculaire connue par ailleurs et un terme σ_c dû à la composition. SUEOKA *et al.*[51] calculent σ_c pour plusieurs acides nucléiques.

Dans ce domaine, nous citerons également l'étude d'homopolymères constitués de séquences isotactiques et atactiques. Il n'y a pas ici de polydispersité de composition chimique, mais une polydispersité de structure. Celle-ci va entraîner une polydispersité des volumes spécifiques partiels pour les mêmes raisons que la polydispersité chimique.

L'étude de polystyrène riche en séquences isotactiques a été faite par plusieurs auteurs[52,53]. Il est également possible de faire une analyse plus fine de la courbe de distribution des concentrations du copolymère dans la cellule. On peut, en utilisant une méthode mathématique proposée par HERMANS[54], obtenir la courbe de distribution des masses spécifiques du copolymère. Il faut pour cela, déterminer la répartition des masses moléculaires par une autre technique. Ce procédé a été appliqué une seule fois jusqu'à présent à notre connaissance[55] à 2 échantillons d'acide désoxyribonucléique. Bien que le calcul de HERMANS ait résolu le problème dans son principe, la méthode est encore très délicate à mettre en oeuvre et elle est susceptible d'un certain nombre d'améliorations en ce qui concerne la précision des courbes expérimentales, leur extrapolation à dilution infinie, et les calculs numériques qui bénéficieront dans l'avenir de l'utilisation routinière d'ordinateurs.

En résumé, il faut dire que cette technique d'E.S.G.D. n'en est qu'à ses débuts d'applications aux copolymères de synthèse. Quand un certain nombre de perfectionnements y auront été apportés, ce sera certainement une des méthodes, si ce n'est la méthode par excellence, pour l'étude des copolymères.

Equilibre en gradient de densité; méthode préparative

Cette méthode sert beaucoup en biochimie. Son principe est le même que celui que nous avons décrit précédemment. Pratiquement, elle se fait à l'aide d'une centrifugeuse préparative, munie d'un rotor avec des godets oscillants. A l'arrêt de la machine, on perce les tubes de centrifugation dans leur partie inférieure et on recueille un certain nombre de fractions que l'on analyse par d'autres méthodes telles que l'électrophorèse, la diffusion de la lumière, la spectrophotométrie d'absorption, etc.

L'application de cette méthode aux polymères et aux copolymères de synthèse serait intéressante à plusieurs points de vue.

Les tubes de centrifugation préparative sont plus longs que la cellule de mesure de la centrifugeuse analytique. La vitesse de rotation utilisée pouvant être la même (40,000 tours/min) on pourrait donc étudier des bandes de polymère plus larges, donc des masses plus faibles s'il s'agit d'homopolymères, des distributions de composition plus larges pour les copolymères.

Si on a affaire à un mélange de macromolécules, par exemple du copolymère AB et 2 sortes de polymères AA et BB, on pourra séparer les 3 constituants et soumettre les fractions ainsi obtenues à des analyses ultérieures. Ce procédé permettrait aussi de séparer des polymères de stéréorégularité différente.

Enfin, en ce qui concerne le copolymère seul, on peut envisager de faire un fractionnement selon la constitution chimique des molécules. Cette méthode prometteuse n'a pas encore été utilisée à notre connaissance avec des produits de synthèse.

Sédimentation de zone

Là encore, il s'agit d'une technique utilisée avec les produits biologiques[56,57] et dont l'application aux polymères de synthèse serait intéressante. Elle peut se pratiquer en centrifugation analytique et préparative.

Le principe en est le suivant: on remplit la cellule de solvant pur. Au-dessus de cette colonne liquide, on place une couche mince de solution macromoléculaire. Les macromolécules contenues dans cette zone vont alors sédimenter vers le fond de la cellule, et au lieu d'observer une frontière solvant–solution qui migre, on observera une zone de solution qui se déplace. Nous avons dit qu'en principe on remplissait la cellule de solvant pur. En pratique, ceci n'est pas possible. En effet, la couche de solution étant plus dense que le solvant, on aurait une instabilité et un mélange par courants de convection. Pour que la zone, pendant son déplacement, rencontre constamment un solvant plus dense qu'elle, on utilise un mélange (eau–glucose pour les mesures biologiques) et on remplit la cellule de telle facon qu'on ait un gradient de densités croissantes vers le fond de la cellule. Insistons sur le fait que ce gradient est tel qu'il permet toujours la sédimentation des macromolécules. Sa raison d'être est uniquement la stabilisation du système et les conditions ne sont jamais telles que l'on obtienne un équilibre en gradient de densité. La présence de ce gradient est un inconvénient. En effet, la viscosité, la masse spécifique du milieu varient le long de la cellule. De plus, il peut y avoir des interactions entre les macromolécules et le soluté choisi pour réaliser le gradient. Aussi, il est difficile de faire des mesures quantitatives de vitesse de sédimentation par cette technique. Par contre, le pouvoir de résolution de ce procédé est important. Cette méthode présente donc un grand intérêt dans l'analyse de mélanges dont les vitesses de sédimentation sont voisines. Cet avantage est encore plus frappant dans la variante préparative de la méthode. Dans ce cas, étant donné la longueur du parcours, la zone peut se décomposer en plusieurs zones qui pourront être recueillies et étudiées séparément. Il s'agit donc d'une méthode qui s'appliquera à des macromolécules de masse moléculaire assez élevée pour que leur vitesse de sédimentation soit suffisante et pour que la diffusion des zones ne soit pas trop importante.

On peut alors analyser des mélanges et en séparer les constituants. On peut espérer aussi faire des analyses de polydispersité dans certaines conditions.

PERSPECTIVES D'AVENIR DUES À L'EMPLOI DE CALCULATRICES ÉLECTRONIQUES

Depuis plusieurs années une évolution s'amorce, concernant l'application d'une technologie et de moyens de calculs nouveaux à l'ultracentrifugation. Les spécialistes de la centrifugation sont amenés à repenser tout le protocole d'une expérience depuis l'observation du phénomène jusqu'aux calculs numériques permettant d'établir les résultats. **Trautman** a fait le point à ce sujet dans une revue récente[58]. Cet auteur cite les améliorations qui ont déjà été apportées à l'observation du phénomène: cette observation se fait classiquement par photographies sur lesquelles on mesure ensuite des longueurs. Il existe déjà d'une part des systèmes électromécaniques permettant d'éliminer ce procédé[4,59]. On connaît aussi des comparateurs automatiques qui peuvent lire les photographies. En ce qui concerne l'exploitation des données, **Trautman** passe en revue les différents programmes de calcul qui ont déjà été publiés. Il en existe déjà concernant les mesures de vitesse, les mesures d'équilibre par la méthode d'**Archibald** et la sédimentation de zone. Nous pensons que l'apport des calculatrices électroniques sera très intéressant en ce qui concerne d'une part le calcul de la fonction $g(s)$ dont nous avons parlé plus haut, et l'étude de la polydispersité des copolymères par E.S.G.D. En effet, dans ces 2 méthodes, les relations théoriques sont bien connues. Mais l'exploitation de ces techniques n'est pas possible en routine étant donné la longueur et la complexité des calculs numériques. Grâce à un ordinateur, on pourra fair ces calculs rapidement, et on peut même envisager des applications industrielles: on pourra par exemple, suivre l'évolution de la fonction $g(s)$ en cours de fabrication d'un polymère: dans ce cas, le temps sera réduit à la durée de la mise en route de la machine et au début de la sédimentation, temps qui est de l'ordre de l'heure.

On peut alors, comme le fait **Trautman**, prévoir une modification profonde du déroulement des expériences: le faisceau lumineux traversant la où les cellules en cours de centrifugation est analysé directement et l'information ainsi reçue est digitalisée et stockée sur bande magnétique. Puis elle est envoyée à un ordinateur qui la traitera en même temps que les données provenant d'autres appareils et d'autres abonnés. Les données obtenues reviennent alors directement à l'utilisateur, qui peut arrêter l'expérience dès qu'il pense que les résultats obtenus sont suffisants.

C'est certainement là le sens dans lequel les techniques de centrifugation vont évoluer. Mais il faut faire preuve d'un optimisme mesuré dans ce domaine, en particulier à cause des prix très élevés du matériel nécessaire, et on verra certainement longtemps encore des chercheurs travaillant selon les méthodes classiques.

RÉSUMÉ

Après l'exposé des deux techniques de base que sont les mesures de vitesse et d'équilibre de sédimentation en milieu binaire, l'auteur présente les méthodes plus récentes qui ont un point commun: c'est la présence d'un deuxième soluté non macromoléculaire. Leur application aux polymères de synthèse est encore assez rare, mais ne saurait tarder étant donné l'intérêt qu'elle présente. L'usage des ordinateurs simplifiera notablement l'exploitation des résultats et diminuera le temps nécessaire à faire une mesure.

SUMMARY

After a review of the two techniques based on sedimentation rate and equilibrium in binary medium, more recent methods involving the presence of a second non-macromolecular solute are described. Application of these methods to synthetic polymers is still rare but of increasing interest. The use of computers simplifies the exploitation of the measurements.

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SHORT COMMUNICATIONS

Spectrophotometric determination of some aldehydes and ketones with 2,4-dinitrophenylhydrazine

Although there are numerous methods for the colorimetric determination of aldehydes and ketones using 2,4-dinitrophenylhydrazine (DNPH)[1-4] most suffer from very high reagent blanks and color instability. Attempts to correct these problems generally result in procedures which have limited application or involve elaborate purification techniques. The method used in this laboratory can detect traces of aldehydes or ketones in various solvents at concentrations where other methods fail. The method presented below is capable of determining as little as 0.3 p.p.m. of carbonyl compounds. It is particularly useful for determination of acetone in polymer-grade *n*-hexane

Reagents and apparatus

Prepare calibration standards by weighing acetone into acid-washed or "Spectro-Grade" *n*-hexane to obtain standards containing from 0 to 10 p.p.m. acetone.

Prepare DNPH reagent daily by saturating an aqueous 20% (v/v) solution of phosphoric acid (85% by wt.) with DNPH. Filter off excess to obtain the clear DNPH reagent.

Procedure

Add *ca.* 50 ml of the DNPH reagent and 50 ml of the *n*-hexane standard or sample to flasks immersed in a 60° bath. If precautions are taken to prevent evaporation losses, accurate measurement of the volumes is not necessary since the final hydrazone is in the same *n*-hexane solvent that contained the acetone being determined. Shake the flasks for 30 min in the bath. Decant a sufficient amount of the hexane phase for the spectrophotometric determination of the hydrazone. This spectrophotometric measurement is made directly in the *n*-hexane phase without the addition of any other reagents. Use a reagent blank consisting of pure solvent (*n*-hexane) carried through the procedure as the instrument null. When an individual aldehyde or ketone is determined in a certain solvent, use the wavelength of maximum absorbance of that hydrazone in order to attain maximum sensitivity. In the case of acetone in *n*-hexane, this measurement is made at 245 nm.

The method can also be applied to the determination of aldehydes and ketones in water. In this case, add 10 ml of phosphoric acid to 50 ml of the aqueous sample. Add 50 ml of the DNPH reagent and 50 ml of *n*-hexane to the acidified sample in the reaction flask and proceed as described for acetone in *n*-hexane. Here, the sample and hexane volumes must be measured accurately because the original carbonyl compound is in the aqueous phase and the resulting hydrazone is extracted into the *n*-hexane phase.

Results

Results for 5 different carbonyl compounds in *n*-hexane or water are shown

TABLE I

DETERMINATION OF VARIOUS CARBONYL COMPOUNDS

Carbonyl compound	*Solvent*	*Wavelength (nm)*	*Concentration (p.p.m.)*	*Carbonyl oxygen (μg in 50 ml)*	
				Added	*Recovered*
Acetone	*n*-Hexane	345	9.28	128	126
			0.28	3.8	4.8
Acetone	Water	345	3.57	49.3	44.9, 47.7, 48.9
Butanone	*n*-Hexane	348	20.0	222	209, 225, 212
					232, 221
Butanone	Water	348	2.00	22.2	22.4
Cyclohexanone	Water	344	4.85	39.5	41.5, 38.6
Proprionaldehyde	Water	341	3.78	52.1	48.9
			11.3	156	156
n-Butyraldehyde	*n*-Hexane	342	3.07	34.1	34.2, 32.6, 35.9
			0.31	3.4	3.5, 3.8
n-Butyraldehyde	Water	342	4.11	45.6	48.4, 49.4, 47.6

in Table I. The average error for carbonyls at the 0.3–11.3 p.p.m. level is 0.14 p.p.m. The average deviation for replicate analysis is 0.09 p.p.m. A solution of 20 p.p.m. of *n*-butyraldehyde in *n*-hexane gave an average of 19.8 p.p.m. for 5 determinations with a standard deviation of 0.87 p.p.m. As little as 3.4 μg of carbonyl oxygen has been determined with an average error and deviation of less than 0.3 μg of carbonyl oxygen.

Discussion

Method. The conditions outlined in the experimental section have been studied in considerable detail. As others have pointed out[3,4], heat is necessary to drive the DNPH coupling reaction to completion in a reasonable amount of time. Agitation is also necessary in this heterogeneous reaction mixture, since the hydrazine reactant is in the aqueous phase and the hydrazone product is in the *n*-hexane phase. Although acidification of the aqueous phase produces lower blanks[1,2], acid in excess of the 20% used in this method had no effect. In addition to heat, agitation, and acidification, freshly-made DNPH reagent is necessary for maximum sensitivity. The net absorbance caused by 4.1 p.p.m. of butyraldehyde fell from 0.91 absorbance units for freshly-made reagent to 0.20–0.27 for reagent that was allowed to stand on a laboratory bench for two weeks.

By using these reaction conditions and measuring the resulting hydrazones directly without the usual addition of alkali, many of the problems noted in the earlier methods are eliminated. The reagent blanks are low and reproducible and the final color system is stable for at least 24 h.

The method can be extended to include the determination of various aldehydes and ketones in other non-polar, water-immiscible solvents. Solvents used successfully include carbon tetrachloride, chloroform, hexane, iso-octane, and cyclohexane. Aldehydes and ketones in the 0–20 p.p.m. range could not be determined in low molecular weight alcohols and esters, olefins, or aromatics. Failures in these solvents were generally characterized by very high reagent blanks. These high blanks were probably caused by extraction of the DNPH reagent into these solvents.

Since the success of the method depends on the ready extraction of the hydrazones from the DNPH reagent, the method should be readily extended for the determination of more complex, higher molecular weight aldehydes and ketones.

Reagent blanks. Reagent blanks, from several days' analyses obtained by using pure solvent as the instrument null, had an average absorbance of 0.051 with a standard deviation of 0.004 absorbance units. This standard deviation is equivalent to about 0.1 p.p.m. acetone. A typical reagent blank of acid-washed hexane was scanned and found to have an absorption maximum at 326 nm with an absorbance of 0.076 at that wavelength. In addition to being sensitive to the acidity of the aqueous phase, the reagent blanks are also quite sensitive to the DNPH reagent. Although freshly-prepared DNPH reagent produced reagent blanks having absorbances of 0.05, reagent that had been standing for 3 days produced reagent blanks having absorbances of 0.20 to 0.30.

Absorbance maxima. The absorption maxima and the molar absorptivities of the individual 2,4-dinitrophenylhydrazones vary for specific aldehydes and ketones in specific solvents[5]. In order to obtain the highest sensitivity, the wavelength of maximum absorbance and calibration curves of the aldehyde or ketone being determined were used. Although the differences are not great for similar aldehydes and ketones, the separate wavelengths and curves are needed to attain the results shown in Table I. If analyses are needed for trace carbonyls and the aldehyde or ketone present is not known, or if a mixture of carbonyl compounds is present, the absorption measurement at 340 nm suggested by LOHMAN[4] is preferred because of the similarity of the molar absorptivities of various hydrazones at that wavelength.

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The use of mercury(II) bromide as coating in a piezoelectric crystal detector

In a recent article, KING[1] described the use of piezoelectric quartz crystals as detectors in gas chromotography. In this application advantage was taken of the very high sensitivities of the vibrating crystal to the absorption of materials on the crystal surface. The change in the frequency of vibration is proportional to the change in weight due to the presence of a solid on the crystal surface, according to the equation:

$$\Delta F = 2.3 \cdot 10^6 \cdot F^2 \cdot \Delta W / A$$

where ΔF is the frequency change due to a coating, in counts/sec; F the frequency of the quartz plate in Mc; ΔW the wt. of the deposited film, in g; and A the area of the quartz plate or electrode in cm^2.

Selective detection of a particular vapor can be accomplished through the use of selective coatings. Some of the substrate coatings that have been used include liquids such as sulfolane to detect polar organic compounds, solids, such as silica gel, or alumina for the measurement of water vapor, and metal films and salts, such as silver, copper and lead acetate for the detection of hydrogen sulfide[1].

Preliminary results revealed that mercury salts could be used as coatings on a piezoelectric crystal for the determination of organophosphorus compounds. An IR study of the interaction of these gaseous compounds with solid transition metal salts was undertaken to ascertain the nature of this interaction.

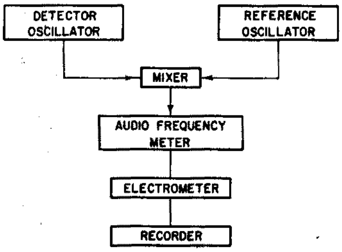
Materials

Diisopropylmethyl phosphonate (DIMP, Mobil Chemical Company) was purified by vacuum distillation, and was used as a model organophosphorus compound. A constant pressure of DIMP was maintained by a carbon tetrachloride–nitrogen slush bath, in order to obtain low pressures of the DIMP vapor introduced to the IR cell and to the crystals.

Solutions of mercury(II) bromide, chloride and iodide were prepared in ether at concentrations of 0.01 *M*. The crystals were coated by dipping them in the ether solution, and the weight of the coating was determined by weighing the crystal on a semi-micro analytical balance.

Apparatus

Crystals. The piezoelectric crystals used were 9 or 14 Mc Quartz crystals with a plated metal electrode, AT cut in a HC 6/U holder (Piezoelectric Crystal Co., Carlisle, Pa.). The crystals were oscillated at the desired frequency using a Pierce oscillator circuit[2]. The two oscillator frequencies were fed to a mixer where the difference in frequency between the two crystals was obtained. This frequency difference was displayed using an audio frequency meter-electrometer-recorder (Fig. 1).



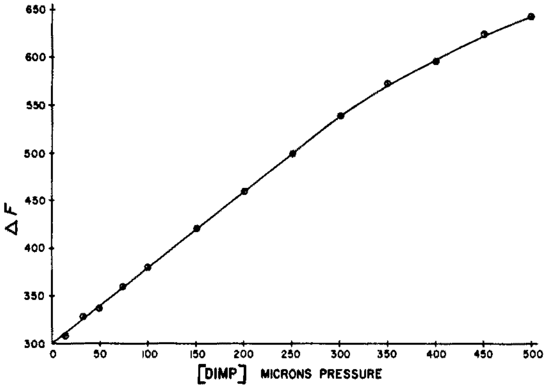


Fig. 1. Schematic of frequency measurement and display.

Fig. 2. Variation of change in frequency, ΔF, with change in [DIMP] vapor concentration expressed in microns of pressure.

Infrared cell. The infrared cell used for the study of gas solid reactions was constructed from stainless steel and had a path length of 0.5 cm. Windows used for the infrared cell were 1-in diameter KBr plates. The KBr windows were sealed to the cell using indium O-rings as described by SMILEY[3]. All gases were introduced into this cell at high vacuum (10^{-6} mm) using a conventional manifold.

Piezoelectric crystals

Two 9- or 14-Mc coated quartz crystals were placed on a high vacuum line and a pressure of 10^{-6} mm of mercury was achieved. The frequency difference between the two crystals was adjusted to *ca.* 300 cycles. One crystal, the reference crystal, was held at high vacuum, and a known pressure of highly purified compounds was then introduced to the second crystal, the detector crystal. Calibration plots were constructed of the change in frequency, ΔF, *versus* the pressure of the gas introduced (Fig. 2).

Infrared experiments

A thin, homogeneous layer of the transition metal salt was deposited onto the KBr windows of the infrared cell by evaporation from ether solution. The KBr plate was quickly placed into the vacuum cell, which was evacuated to remove any traces of moisture, and an infrared spectrum was recorded using a IR-7 spectrophotometer. The cell was again placed on the vacuum manifold and evacuated, followed by an introduction of the DIMP. After interaction for 90 min, the cell was removed from the manifold and a second infrared spectrum obtained. If there was an interaction, as evidenced by the appearance or shift of bands, the cell was again evacuated for a period of at least a day, and a spectrum again obtained, in order to determine whether the interaction was chemical or physical in nature.

Ordinarily a path length of 0.5 cm will not produce a visible spectrum of a gas because there are too few molecules present. In order to note any changes in the spectrum of the organophosphorus compound resulting from its interaction with the solid, it was necessary to obtain a gas spectrum of the organophosphorus compound alone in a cell of 10 cm path length. An infrared spectrum of the organophosphorus compound in the liquid phase was also obtained to aid further in the assignment of bands.

Alternatively, experiments using KBr pellets were performed in the following manner. Crystals of the transition metal salts were placed in a reaction finger attached to a vacuum line, and the system was evacuated to 10^{-6} mm Hg. The infrared spectra of the KBr pellets of the salts were recorded both before and after reaction with DIMP. IR measurements were made after pumping the phosphonate from the reaction cell and sampling the transition salt–diisopropyl methyl phosphonate product.

Discussion and results

The response of two uncoated 14-Mc quartz crystals to various compounds was studied to achieve some idea of the effectiveness of using specific films to coat the crystal. Application of a large concentration (2 mm pressure) of DIMP to an uncoated 14-Mc crystal produced a change in frequency of only 75 cycles, and water (3 mm) produced a 25-cycle change. Both materials were quickly removed from the crystal on application of vacuum, and the frequency returned to its original value, indicating physisorptions.

Initially, extreme difficulty was encountered in attempting to put coatings onto the crystals and yet keep them oscillating at a small frequency difference. The best technique found was to quickly dip both crystals once into a 0.01 *M* solution of the coating material. By this technique, mercury(II) bromide was coated onto two 14-Mc crystals, both crystals were brought to 10^{-6} mm pressure, and then either water vapor, oxygen, air or DIMP was introduced onto the crystal. A total frequency change of 400 cycles resulted from the application of 0.7 mm of the phosphonate molecule. Large quantities of air and oxygen (25 mm) caused little change in the frequency of the crystal (20 cycles). Large amounts of water vapor (25 mm) caused a 100 cycle change in the frequency of oscillation. It may be concluded from this that mercury(II) bromide is a good coating for the determination of organophosphorus compounds. Fair linearity exists with a limit of detection of 10^{-4} mm of material (Fig. 2). Upon application of a vacuum, water vapor, oxygen and air were very quickly removed from the crystal, indicating physisorption. The phosphonate, however, was removed only with difficulty, and the base frequency was never reachieved, indicating chemisorption.

TABLE I

CHANGE IN THE P→O STRETCHING FREQUENCY UPON INTERACTION OF DIMP VAPOR WITH VARIOUS TRANSITION METAL SALTS

Interactants	*Frequency* (cm^{-1})	$\Delta\gamma$(cm^{-1})
DIMP (Liquid)	1246 (s)	
DIMP (Vapor)	1265 (s)	—
DIMP + $MnCl_2$	1198 (s), 1220 (sh)	67
DIMP + $CuCl_2$	1185 (s), 1200 (sh)	80
DIMP + $ZnCl_2$	1173 (s), 1205 (sh)	92
DIMP + $HgBr_2$	1176 (s), 1225 (w)	89
DIMP + $HgCl_2$	1228 (s), 1174 (w)	37

s = strong, w = weak, sh = shoulder.

The sensitivity of response was next studied, as a fraction of the weight of the coating and of the frequency of the crystal used. In general, there was an increase in the ratio of ΔF/(mm of DIMP) with increasing weight of the coating used in the range studied (0.1–2 mg). The 9-Mc crystal appeared less sensitive than the 14-Mc one (ΔF of 250 cycles for 0.7 mm of DIMP for a 9-Mc crystal compared to 400 cycles for a 14-Mc crystal).

It was discovered that salts of heavy metal transition elements, $HgCl_2$, $HgBr_2$, $MoCl_5$, $CuCl_2$, $MnCl_2$, and $ZnCl_2$, exhibited a strong chemical interaction with DIMP, as evidenced by a frequency shift to lower wave numbers of the phosphoryl stretching vibration. This indicated that a complex had been formed between the inorganic salt and the organophosphorus vapor at the site of the phosphoryl oxygen. Attempted evacuation of the cell after interaction resulted in no change in the infrared spectrum, indicating that a chemisorption reaction had occurred. There appeared to be a trend in the amount of the shift of the phosphoryl stretching frequency and hence in the bonding strength between the phosphoryl group and the metal salt. Some values of the phosphoryl stretching frequency and the change in frequency, $\Delta\gamma$, are given in Table I. No change in the P–O–C band frequency was found in these studies. Hence, salts of most transition metals should prove useful as coatings in a piezoelectric crystal detector, and results obtained using these salts as coatings on a piezoelectric crystal used as a gas chromatographic detector will be published later.

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Spectrophotometric determination of palladium(II) with isonitrosoacetophenone

Isonitrosoketones react with metal ions to give colored complexes[1] which can be extracted into organic solvents. TALWAR AND HALDAR[2] have shown that isonitrosoacetylacetone can be used for the extraction and spectrophotometric determination of palladium. The analytical applications of the colored compounds of isonitrosoacetophenone with metals other than iron have not been investigated. The present paper describes a rapid method for spectrophotometric estimation of microgram quantities of palladium with isonitrosoacetophenone.

Apparatus

Absorbance was measured either on a Hilger ultraviolet spectrophotometer or on a Unicam Colorimeter, Model SP 300, using 1-cm silica cells. pH measurements were taken with a Elico pH-meter LI 10 (Electronic and Industrial Instruments Co., Hyderabad).

Reagents

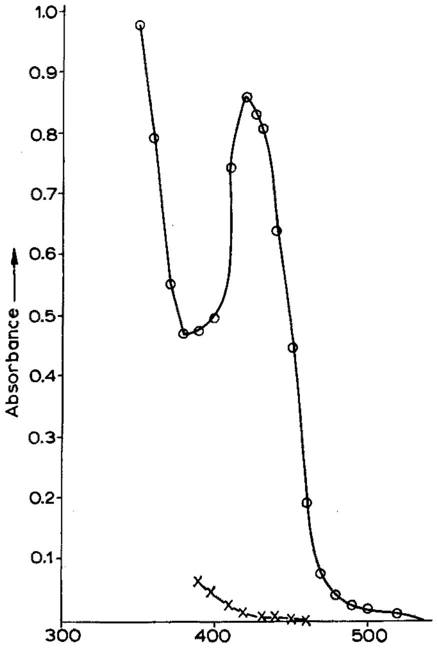
Reagents and chemicals used were of A.R. quality. All solutions were made in double-distilled water prepared in an all-glass apparatus. Palladium stock solution was prepared by dissolving palladium chloride in a minimum volume of concentrated hydrochloric acid and diluting suitably; it was standardized by the dimethylglyoxime method[3]. Isonitrosoacetophenone was prepared as described by WELCHER[4]. Solutions for the interference study were obtained by dissolving appropriate salts in water to give 20 mg of the element per ml.

General procedure

Transfer 1 ml of palladium solution containing 1–100 μg Pd to a 30-ml separatory funnel and adjust the acidity to 0.1–1 *N* in acetic acid, keeping the total volume of the solution to 10 ml. Add any masking agents necessary before adjusting the acidity. Equilibrate for 2 min with 8 ml of 0.1% reagent solution in benzene. After the separation of the two phases, transfer the organic phase to a 10-ml measuring flask, and wash the aqueous phase with 2 ml of benzene. Dilute to the mark, if necessary, with benzene. Measure the absorbance of the solution at 420 nm, using a reagent blank. Determine the amount of palladium from a calibration curve.

Results and discussion

It was found that 1–100 μg of palladium was quantitatively extracted into benzene by a single extraction with 8 ml of 0.01–0.1% isonitrosoacetophenone solution in benzene. The yellow benzene extract showed a strong absorption maximum at 420 nm (Fig. 1); the absorbance of the 0.1% reagent solution was less than 0.005. Beer's law was obeyed in the range 0.1–10 μg of Pd per ml of final solution. The molar extinction coefficient of the colored species at 420 nm was 10,345 mol^{-1} cm^{-1}, calculated on the basis of total palladium. The color development was instantaneous and the absorbance of the benzene solution was stable for 6 h. No interference



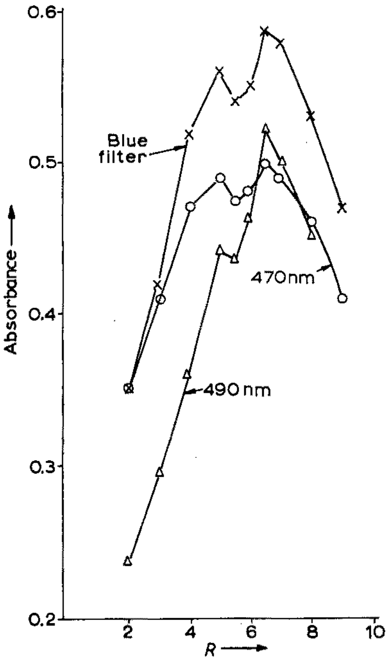


Fig. 1. Absorption spectrum of palladium–isonitrosoacetophenone. 50 μg of Pd extracted from 10 ml 1 *N* acetic acid solution with 10 ml of 0.1% isonitrosoacetophenone in benzene. (×) 0.1% isonitrosoacetophenone in benzene.

Fig. 2. Job's continuous variation plot. R = volume of reagent solution added; Pd solution + reagent solution = 10 ml. Absorbance measured after extracting color from 1 *N* acetic acid solution with 10 ml of benzene. (×), (△), 0.00185 *M* solution of each reactant; (○) 0.0037 *M* solution of each reactant.

by milligram amounts (indicated in parentheses) of the following ions was observed: Pt^{4+} (20) as $PtCl_6^{2-}$, Pt^{2+} (20) as $PtCl_4^{2-}$, Rh^{3+} (20), Ru^{3+} (20), Ir^{4+} (20) as $IrCl_6^{2-}$, Os^{8+} (20), Au^{3+} (10), Fe^{3+} (20), V^{5+} (20), Cr^{3+} (20), Cr^{6+} (10) as CrO_4^{2-}, Mn^{2+} (20), Co^{2+} (20), Ni^{2+} (20), Cu^{2+} (20), Zn^{2+} (20), La^{3+} (20), Al^{3+} (20), Ce^{3+} and Ce^{4+} (20), U^{6+} (20) as UO_2^{2+}, Re^{7+} (20) as ReO_4^-, W^{6+} (20) as WO_4^{2-}, Mo^{6+} (20) as MoO_4^{2-}, Th^{4+} (20), Zr^{4+} (20), Cd^{2+} (20), Hg^{2+} (20), Sn^{2+} (20), Se^{6+} (50) as SeO_4^{2-}, Be^{2+} (20), Mg^{2+} (20), Ba^{2+} (20), Ca^{2+} (20), Sr^{2+} (20), Pb^{2+} (20), Li^+ (20), As^{5+} (20) as AsO_4^{3-}, SO_4^{2-} (100), NO_3^- (100), Cl^- (40), Br^- (50), F^- (excess), PO_4^{3-} (100), pyrophosphate (excess), BrO_3^- (excess), ClO_4^- (100), oxalate (20), tartrate (excess), citrate (excess), persulfate (excess), NH_2OH (20), urea (excess), N_2H_4 (excess). Chloride (>40 mg) and cyanide could be masked with mercury(II) nitrate, sulfide and sulfite with permanganate and sulfuric acid, thiosulfate with sodium molybdate and hydrogen peroxide, and EDTA with copper sulfate. In the absence of chloride, silver did not interfere. Iodide was removed by boiling the solution with potassium persulfate and nitric acid before adjusting the acidity of the solution with acetic acid.

The absorbance of the benzene solution was not affected by extracting the yellow species from 0.5 N sulfuric, perchloric, nitric or phosphoric acid solution but the tolerance limit for hydrochloric acid was 0.1 N due to the interference by excess of chloride ions. Chloroform or toluene solution of the reagent could be used for color development.

Composition of the extracted species

Job's continuous variation method[5] as adapted by IRVING AND PIERCE[6] for two phase systems, was employed to establish the composition of the extracted species. The curves (Fig. 2) obtained with equimolar solutions indicate 2 maxima at ratios of Pd: isonitrosoacetophenone equal to 1:1 and 1:2, corresponding to the formation of $Pd(INAP)^+$ and $Pd(INAP)_2$ respectively. It may, therefore, be inferred that in the presence of excess reagent, the color is due to the neutral species $Pd(INAP)_2$.

Precision, accuracy and sensitivity

Solutions containing known amounts of palladium were analysed by the above procedure. With 5.00 µg of Pd per ml, the average of 10 results was 5.02 µg, the variation from the mean being ±0.06 at the 95% confidence limit. The sensitivity of the method, as defined by SANDELL[7], was 0.01 µg which is comparable to other known methods. The chief advantages of the proposed method are that ions, other than iodide, do not interfere, rigid control of pH of the aqueous solution is not required, and the color development is rapid. The practical sensitivity can be increased by extracting the colored species into a smaller volume of benzene.

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Anal. Chim. Acta, 39 (1967) 264–267

A rapid empirical method for the simultaneous determination of hydroxyl and aluminium in aluminate and basic aluminium nitrate solutions

The reprocessing of irradiated reactor fuel elements by means of chemical decladding begins with dissolution of the fuel element cladding, and then dissolution of the uranium fuel core. Fuel elements clad in aluminium are declad by means of a sodium hydroxide solution; the final solution is about 1.5 *M* in sodium aluminate and 2.5 *M* in sodium hydroxide. Another type of fuel element consists of an aluminium–uranium alloy with a molar ratio of aluminium to uranium of 260. These fuel elements can be dissolved completely in nitric acid to give a basic aluminium nitrate solution, which is about 1.8 *M* in aluminium and 1 *M* in hydroxyl. The hydroxyl and aluminium concentrations have to be determined for process control; analyses must be done in lead-shielded air-tight boxes because of radiation hazards.

The method described below for the simultaneous determination of the two constituents is based on a potentiometric titration with sodium hydroxide solution after addition of excess nitric acid to neutralize the hydroxyl. The amounts of base corresponding to relevant points of inflexion in the titration curve are empirically related to the concentrations of the two constituents.

Standard solutions

Two aluminate solutions, differing in free base concentration, were used as standards. The solutions were prepared by dissolving a known amount of aluminium metal in a known amount of sodium hydroxide, assuming the following reaction:

$$Al + n\ OH^- + 3H_2O \rightarrow [Al(OH)_4]^- + (n-1)\ OH^- + \tfrac{3}{2}\ H_2$$

The molar ratios of total hydroxyl to aluminium for the solutions were 5.7 and 5. The second standard was not stable for very long.

A solution of basic aluminium nitrate was prepared by dissolving a known amount of aluminium in nitric acid in the presence of a little mercury(II) nitrate as catalyst, yielding a solution with a molar ratio of hydroxyl to aluminium of about 2.

Procedure

Aliquots of the solutions were pipetted into the titration vessel and 0.500 ml of concentrated nitric acid was added. After 5 min, the solution was diluted to a volume of 50 ml. The approximate aluminium contents in the titration vessel were about 0.30, 0.45, 0.60, 0.75 and 0.90 mg-atoms. The solutions were titrated in duplicate with standard 0.500 *N* sodium hydroxide solution by means of a recording titrator (Metrohm E 336), which has a motor-driven syringe and which was connected to a combined glass–calomel electrode (Metrohm EA/121/UX). Stirring was required. The titrator records the derivative of the titration curve; the peaks correspond to the relevant points of inflexion of the titration curve. The amounts of base added can be read to 0.005 meq.

Results and discussion

The derivative titration curve shows 2 peaks (see Fig.1). The amounts of base added up to the first peak and between the first and second peaks correspond mainly to the neutralization of the hydroxonium ions and the precipitation of aluminium hydroxide. Preliminary investigations showed that the nitrate concentration influences the position of the first and second peaks. A constant amount of about 7 mmol of nitric acid is therefore added in each titration.

As can be seen in Fig. 1, the second peak has a slight foot, the slope of which is more pronounced with high aluminium concentrations and incomplete neutralization.

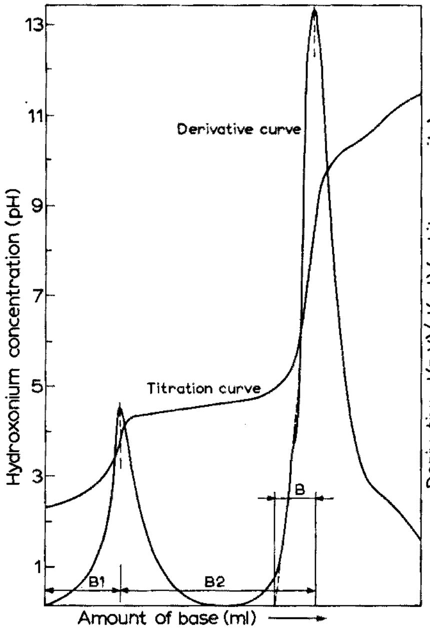

Fig. 1. A typical example of a recorded titration curve.

The slope can be expressed by the distance B on the horizontal through the lowest point between the two peaks. The addition of concentrated nitric acid and a waiting time are essential for complete neutralization of the hydroxyl–aluminium complexes, particularly for the dibasic aluminium nitrate solution; the use of dilute acid requires a long waiting time and heating. A criterion can be found by calculating the ratio B^2/B_2. The neutralization can be considered complete if the ratio is less than 0.09.

Linear regression analysis[1] of the 20 sets of data obtained by titration of the two aluminate solutions, with the amount of aluminium (Al mg-atoms) present in the titration vessel and the amount of base for hydroxide precipitation (B_2 meq) as variables, gave the equation:

$$Al = 0.3614\ B_2 \qquad (1)$$

An unknown aluminium concentration in an aluminate or basic aluminium nitrate solution can therefore be calculated if the amount B_2 is determined. On the basis of replicate analyses of known solutions, the relative standard deviation was found to be 0.3–0.4% depending on the amount present.

The nitric acid (A meq) added to an aliquot of an aluminate solution neutralizes the free base (OH meq) and the hydroxyl–aluminium complexes (4 Al meq) and the excess of nitric acid is back-titrated with base (B_1 meq). Analysis of the 20 sets of data showed a difference of 0.085 meq (standard deviation $1.9 \cdot 10^{-2}$ meq) between B_1 and the expected amount, which was independent of the aluminium concentration. The following equation is valid:

$$OH = 0.085 + A - B_1 - 4\ Al \qquad (2)$$

The term 4 Al is related to the amount of base for hydroxide precipitation (B_2 meq) according to eqn. (1). Substitution in eqn. (2) gives the relationship between the amount of free base present in the titration vessel and the two measurable variables:

$$OH = 0.085 + A - B_1 - 1.446\ B_2$$

For an aliquot of a basic aluminium nitrate solution, the acid added neutralizes the hydroxyl–aluminium complexes (OH meq) only and the excess is back-titrated. The relationship for the amount of hydroxyl present in the titration vessel is therefore:

$$OH = 0.085 + A - B_1$$

The amount A has to be determined with the titrator so that $A - B_1$ is unbiased. The standard deviation of a free base or hydroxyl determination was found to be $2 \cdot 10^{-2}$. The relative standard deviation is therefore 1–6% for the free base determination and 1–3% for the hydroxyl determination for the concentrations investigated.

The coefficients of the equations are valid for the experimental conditions described and should be redetermined for each experimental arrangement.

Alkalimetric titration with sodium hydroxide couples with potentiometric indication can be used for the determination of many cation mixtures[2]. The method described is easily adaptable to remote control, enables full use to be made of expensive laboratory space, and gives a quick and sufficiently precise analysis.

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Interference from natural radioactivity in neutron activation analysis for bismuth in lead

A number of interferences can severely influence the accuracy of neutron activation analysis. Among these are deviations in neutron density, neutron self-shadowing in samples or standards, second-order interferences, or the occurrence of threshold reactions whereby the matrix element or a minor constituent of the sample can also give rise to the isotope used for the determination. In the case of the determination of bismuth in lead a particular source of interference has not, to our knowledge, been mentioned or investigated before. Naturally occurring ^{210}Bi, a member of the ^{238}U series, can interfere with the ^{210}Bi formed by neutron activation from the ^{209}Bi(n,γ)^{210}Bi reaction. This isotope is always present in variable concentration in recently fabricated lead as a result of the occurrence of uranium in lead ores. Through the manufacturing process, the series is interrupted at ^{210}Pb so that the ^{210}Bi activity decays with the half-life of ^{210}Pb, namely 21 years. Although traces of thorium are also present, no radioisotopes originating from this series are to be expected when several days have elapsed since the fabrication of the lead. An analysis based on the 138-day ^{210}Po daughter of ^{210}Bi is for the same reason also subject to errors; the error is even enhanced in this case.

TABLE I

^{210}Po ABSOLUTE DISINTEGRATION RATE IN LEAD

Sample no.		*Absolute disintegration rate*	
		^{210}Po/g lead (d.p.m.)	*^{210}Bi/g lead (d.p.m.)*
Sample I	1	154.5 ± 2.6	—
	2	152.8 ± 2.3	—
	3	151.5 ± 2.3	—
	4	153.4 ± 2.4	—
Sample II	1	35.6 ± 0.9	—
	2	32.9 ± 0.6	—
	3	33.1 ± 0.6	—
	4	32.0 ± 0.6	—
	5	32.2 ± 0.6	—
Sample III	1	17.6 ± 0.5	18.8
	2	17.8 ± 0.2	
Sample IV	1	35.8 ± 0.6	30.0
	2	37.4 ± 0.7	

The natural radioactivity of ^{210}Po was determined in lead so that the error in the activation analysis for bismuth could be estimated. The method will be described in detail elsewhere; the results of the analyses of 4 recently manufactured lead samples are given in Table I. Two samples were also analysed by measurement of the ^{210}Bi activity after precipitation as BiOBr[1]. The ^{210}Bi disintegration rate must be equal to the polonium-210 disintegration rate, for equilibrium can be expected to exist between the isotopes of the ^{210}Pb–^{210}Bi–^{210}Po chain in all cases. About two years are needed for the full ingrowth of ^{210}Po from ^{210}Pb. It appears from the results that this assumption is correct, as the disintegration rates of ^{210}Po and ^{210}Bi are approximately the same.

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It can be derived directly from these determinations that the naturally occurring radioisotope content of lead differs greatly from one sample to another. The interference from these activities in neutron activation determinations can be very high, especially when a rather low neutron flux is used for the activation. In the case of the sample with the highest ^{210}Pb content (sample no. 1) the interference in the determination of 1 p.p.m. of bismuth at a neutron flux of 10^{12} n·cm^{-2}·sec^{-1} irradiated during 10 h is almost 100% when the bismuth is separated immediately after the irradiation. A waiting time of a couple of days increases the interference, since the specific activity of the ^{210}Bi formed by the activation decays with a half-life of 5.0 days whereas the natural ^{210}Bi activity remains constant. If ^{210}Po is used for the determination in the same conditions of activation, the error made becomes dramatically high, namely 2600%. This is primarily due to the difference in half-lives between ^{210}Po and ^{210}Bi.

The activation analysis of bismuth through the measurement of ^{210}Po is theoretically preferable, because of the advantages in selectivity and sensitivity of the detection of an α-particle instead of β-measurement. However, in the case of bismuth determinations in lead by counting of the ^{210}Po daughter, the sensitivity is limited by the above mentioned interference. One possibility of increasing this sensitivity would be to separate the bismuth from the lead after the irradiation followed by a separation of the ^{210}Po daughter ingrown from the total ^{210}Bi activity. This can easily be understood when the following reactions are considered:

From the ^{238}U series:

$$^{210}\text{Pb} \xrightarrow[21\ \text{y}]{\beta^-,\ \gamma} {}^{210}\text{Bi} \xrightarrow[5.0\ \text{d}]{\beta^-} {}^{210}\text{Po} \xrightarrow[138.4\ \text{d}]{\alpha} \underset{\text{stable}}{{}^{206}\text{Pb}}$$

Equilibrium activity ratio ^{210}Bi to ^{210}Po = 1.

From neutron activation:

$$^{209}\text{Bi} \xrightarrow{n,\ \gamma} {}^{210}\text{Bi} \xrightarrow[5.0\ \text{d}]{\beta^-} {}^{210}\text{Po} \xrightarrow[138.4\ \text{d}]{\alpha} \underset{\text{stable}}{{}^{206}\text{Pb}}$$

^{210}Bi activity after irradiation to maximal activity of ^{210}Po ingrown = 32. (This holds only when the irradiation time is $\ll T_{\frac{1}{2}}$ of ^{210}Bi.)

A nomograph allowing the calculation of the error is represented in Fig. 1 and is applicable for natural ^{210}Po (or ^{210}Bi) activities per gram of lead from 5 to 500 d.p.m. (axis 5). Axis 2 represents the activity produced as a function of neutron flux (axis 1) and irradiation time in hours (axis 4). The activity of ^{210}Bi in d.p.m. is the value obtained at the end of the irradiation whereas the ^{210}Po activity (d.p.m.) is the maximal daughter activity, *i.e.* after a waiting time of *ca.* 25.1 days. The error from either a ^{210}Bi or ^{210}Po measurement is found on axis 3.

Example

An irradiation time of 10 h at a flux of 10^{12} n·cm^{-2}·sec^{-1} for 1 g of lead containing 1 p.p.m. of bismuth will yield 183 d.p.m. ^{210}Bi or 5.7. d.p.m. ^{210}Po. If the sample contains 150 d.p.m. of natural ^{210}Bi or ^{210}Po the error will be respectively 82% and 2600%.

For long irradiation periods the error on the polonium determination shown in the nomograph is not exact, because of the ingrowth of ^{210}Po during the irradiation.

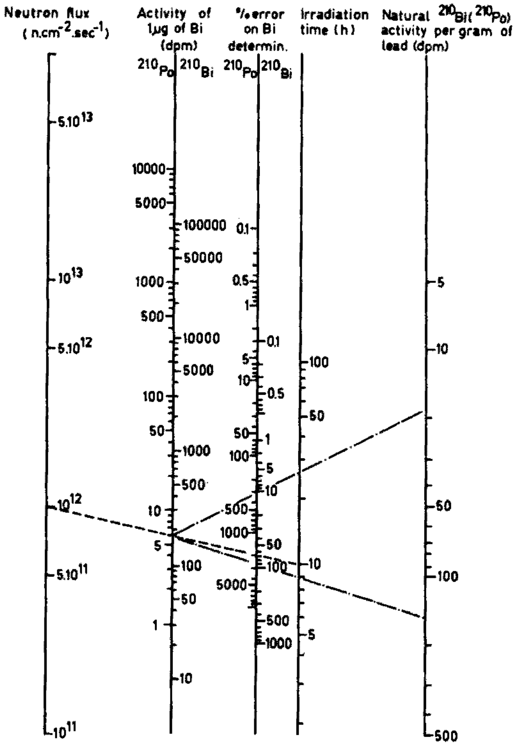

Fig. 1. Error on the bismuth determination by the measurement of ^{210}Bi or ^{210}Po.

For irradiation times of 100 h and 50 h, the results are respectively 37% and 11% too high.

To minimize the interference, either the neutron flux can be increased, or the natural ^{210}Bi or ^{210}Po content of the sample can be determined and subsequently subtracted from the results found.

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Effect of amines on atomic absorption analyses

Numerous references can be cited from the literature showing the interference of various inorganic anions on atomic absorption analyses[1–4]. DAVID[5] and WILLIS[6] have devised chemical methods of removing these interferences. Organic anions can affect the analyses also, usually by increasing the sensitivity for the particular metal involved. ROBINSON[3] states that the organic addend burns in the flame (liberating the metal more easily), leading to a greater absorption signal. HALLS AND TOWNSHEND[7] list EDTA and 8-hydroxyquinoline as organic addends which enhance the absorption of magnesium in an air–propane flame. No reports have been found of organic addends which do not dissociate in the flame.

This study deals with the inhibitory effect exhibited by various amines on the absorption signal of several metal ions. This effect is serious enough to cause an error of 40% in cobalt analyses performed on ethanol solutions which contain only 6% triethylamine.

Apparatus and solutions

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a recorder readout assembly was used in these studies. The instrument was set up for use with either an air–acetylene or nitrous oxide–acetylene flame.

Amines. Triethylamine was purified by distillation. Trimethylamine, diethylamine, dimethylamine, ethylamine, methylamine, aniline, and pyridine were commercially available and these materials were used without further purification. Several of the amines were available as aqueous solutions and trimethylamine was available as a methanol solution.

Standard solutions. The standard solutions of the metal ions were prepared by diluting Fisher "Certified" Atomic Absorption Standards with absolute ethanol. The standards containing amines were diluted with absolute ethanol before adding the respective amine. The percentage composition of the solvents is with respect to volume.

General procedure

Instrument conditions for the analyses of the metal ions were similar to those recommended in the Perkin-Elmer *Analytical Methods for Atomic Absorption Spectrophotometry*. A base-line shift was observed when water was present in the ethanol solutions. This was compensated for by measuring the absorbances with respect to the particular solvent of the sample. The amine solutions (in the absence of water) showed no base-line shift. No change in the flame height was observed when ethanol solutions of the amines were aspirated. The absorbance readings were corrected for aspiration rates different from that for absolute ethanol.

Effect of 6% triethylamine on metal analyses

In ethanol solutions. Standard 10-p.p.m. solutions of iron, cobalt, nickel, chromium, and copper were prepared in absolute ethanol and in ethanol containing 6% triethylamine. The effect of triethylamine on the analyses can be seen in Table I. The amine was found to have essentially no effect on the chromium analysis, caused a slight decrease in signal for copper, caused a considerable decrease for iron and nickel, and caused a drastic decrease in the signal for the cobalt analysis. The cobalt analysis in Table I was performed at 240.7 nm; the same effect on the cobalt analysis was found at 252.0 nm.

The decrease in absorption signal is attributed to a complexing effect by the triethylamine on the metal ion, rather than to a solvent effect in the aspiration and atomization steps. If it were simply a solvent effect causing decreased sensitivity, then chromium should be affected as well as the other metal ions. Also, one would expect the effect to be about the same for all 5 of the metal ions[1] rather than the wide variance which this study reveals.

TABLE I

EFFECT OF 6% TRIETHYLAMINE IN ETHANOL[a]

Solution	*Absorbance*				
	Fe	*Co*	*Ni*	*Cr*	*Cu*
10 p.p.m. metal in EtOH	0.204	0.124[b]	0.167	0.143	0.350
10 p.p.m. metal in 6% TEA–94% EtOH	0.184	0.076[c]	0.141	0.148	0.336

[a] Aspiration rate was 2.3 ml/min for all samples.
[b] 0.070 at 252 nm.
[c] 0.038 at 252 nm.

TABLE II

EFFECT OF 6% TRIETHYLAMINE WITH NITROUS OXIDE–ACETYLENE FLAME[a]

Solution	*Absorbance*		
	Co	*Ni*	*Fe*
10 p.p.m. metal in EtOH	0.051	0.054	0.076
10 p.p.m. metal in 6% TEA–94% EtOH	0.048	0.049	0.074

[a] Aspiration rate was 2.9 ml/min for all samples.

With a nitrous oxide–acetylene flame. It seemed probable that a metal organic complex would dissociate into metal atoms at the temperature of the air–acetylene flame. However, the results indicate that this is not the case with triethylamine. Therefore, it was decided to perform the cobalt, nickel, and iron analyses with the nitrous oxide–acetylene flame. The results of these analyses are shown in Table II. Very little effect was observed; the increased temperature of the nitrous oxide–acetylene flame appeared to dissociate the complex formed with triethylamine. Admittedly, the sensitivities were much lower than with the air–acetylene flame, probably because of increased ionization and oxide formation. However, when the results are compared with those obtained for cobalt at 252 nm in the footnote to Table I (low sensitivity was also involved), it is obvious that the conclusion regarding complex formation between triethylamine and the metal ions is valid. It is assumed that cobalt forms a very strong complex with triethylamine while chromium either forms a very weak complex or none at all. The other metal ions are somewhere in between these two extremes.

Effect of various amines on metal analyses in ethanol solutions

After the effect of triethylamine on cobalt analyses in ethanol solutions had been observed, it was decided to investigate other amines in order to determine whether this effect was characteristic of them as a group. The results are shown in Table III. Trimethylamine, diethylamine and methylamine were found to have considerable effect on the cobalt analyses in ethanol solutions. Dimethylamine and pyridine were found to have a lesser effect. Ethylamine and aniline had essentially no effect.

TABLE III

EFFECT OF VARIOUS AMINES ON ABSORBANCE OF 10 p.p.m. OF COBALT IN ETHANOL SOLUTIONS[a]

Solution	*Aspiration rate*	*Uncorrected absorbance*	*Corrected absorbance*[b]
EtOH	2.3	0.124	0.124
20% H_2O, 80% EtOH	1.7	0.091	0.123
6% Triethylamine, 94% EtOH	2.3	0.076	0.076
12% Triethylamine, 88% EtOH	2.3	0.052	0.052
5% Trimethylamine, 15% MeOH, 80% EtOH	2.5	0.105	0.097
6% Diethylamine, 94% EtOH	2.3	0.084	0.084
6% Dimethylamine, 9% H_2O, 85% EtOH	2.0	0.099	0.114
6% Ethylamine, 12% H_2O, 82% EtOH	1.8	0.094	0.120
6% Methylamine, 9% H_2O, 85% EtOH	2.0	0.083	0.096
6% Aniline, 94% EtOH	2.2	0.116	0.121
6% Pyridine, 94% EtOH	2.3	0.108	0.108

[a] Air–acetylene flame and wavelength = 240.7 nm.

[b] Corrected absorbance = uncorrected absorbance × $\frac{\text{aspiration rate of 10 p.p.m. Co in EtOH}}{\text{aspiration rate of sample}}$

Conclusion

From an analytical standpoint, it is most important to recognize that a number of amines can cause an interference in the atomic absorption determination of metals. This interference appears to be explained by metal–amine complexes which do not dissociate at the temperature of the air–acetylene flame. This effect is best illustrated by the fact that triethylamine at the 6% level in ethanol solutions causes a 40% error in the determination of cobalt. However, the interference can be overcome by using the nitrous oxide–acetylene flame (accompanied by a decrease in sensitivity).

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FRED R. HARTLAGE, JR.

1 W. SLAVIN, A. VENGHIATTIS AND D. C. MANNING, *Atomic Absorption Newsletter*, 4 (1966) 86.
2 A. STRASHEIM AND G. J. WESSELS, *Appl. Spectry.*, 17 (1963) 68.
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5 D. J. DAVID, *Analyst*, 84 (1959) 536.
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7 D. J. HALLS AND A. TOWNSHEND, *Anal. Chim. Acta*, 36 (1966) 280.

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BOOK REVIEWS

H. A. ELION, *Instrument and Chemical Analysis Aspects of Electron Microanalysis and Macroanalysis*, Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 5, Pergamon Press, Oxford, 1966, ix+252 pp., price 90 s.

The definitive work on electron probe microanalysis has yet to be written and—despite the publishers claim on the dust cover—this is certainly not it. The two criteria on which such a book may be judged are: does it contain the essential information and, secondly, does it clearly set out and illustrate this material. This book fails badly on both of these counts.

Predictably, a substantial amount of space is devoted to the Elion DEM 301 microanalyser. This is the only instrument illustrated and appears over the ambiguous caption "The first commercial scanning electron microanalyser built by Elion Instruments Inc.". Unfortunately, it is also memorable for being the only commercial instrument which so far failed to meet its own specification that it quickly went out of production after only a dozen or so had been sold. Both Applied Research Laboratories of California and the Cambridge Instrument Co., England have sold more than 100 instruments—all of which are working and yet no description of either is included apart from a cross-section of the probe-forming lens used in each case.

The dust cover warns that the book goes into particular detail in areas where descriptions in previous publications are lacking. One should therefore be prepared for the fact that five times more space is devoted to the system of afocal electron optics on which the Elion microanalyser depended than is used to describe conventional image-forming systems. The afocal system in principle produces a "parallel" beam of electrons less than 1 μ in diameter which would of course be enormously valuable to the instrument designer in enabling him to use an almost infinite working distance. Unfortunately there is abundant experimental evidence that this system is based on a fallacy, arising from the fact that the current in a parallel beam of electrons would be zero.

One looks in vain, however, for an adequate treatment of essential matters such as the theoretical basis on which the measured intensity ratios are converted into chemical compositions. The most important correction—that for absorption—is particularly skimpily treated on only 2 pages. The most widely used procedure, PHILIBERT's formula, is not even quoted.

It would be wearisome and unnecessary to catalogue further the insufficiencies of this book. Considered either as a useful account of important developments in the field of electron probe microanalysis or as a practical guide to experimental procedures it has nothing whatever to commend it.

D. A. MELFORD (Cambridge)

Polarography 1964, Edited by GRAHAM J. HILLS, Proceedings of the Third International Conference, Southampton, 1964, Macmillan, London, 1966, Vol. I xxviii + 685 pp., Vol. II xxviii + 686–1164 pp., price 315 s. (the set).

Most of the workers prominent in polarography have contributed to the papers included in these volumes. Ninety-one papers cover the whole spectrum of polarographic research, from intricate theoretical problems to interesting analytical applications; key lectures by BARKER, BREYER, FLEISCHMANN, KOLTHOFF, MILAZZO and ZUMAN are included. The book is well produced and edited, and is a useful though very expensive record of the trends in polarographic development 3 years ago.

A. TOWNSHEND (Birmingham)

Analyse der Metalle. I. Band. Schiedsanalysen, 3. neubearbeitete Auflage, Herausgegeben vom CHEMICKERAUSSCHUSS DER GESELLSCHAFT DEUTSCHER METALLHÜTTEN- UND BERGLEUTE E.V., Springer-Verlag, Berlin, 1966, xii + 507 S., Ganzleinen DM 57.—.

La Commission des Chimistes de la Société Allemande des Fondeurs et Mineurs a réédité (3ème édition) son ouvrage traitant de l'analyse quantitative des métalloïdes et des métaux non ferreux destiné plus spécialement aux laboratoires de contrôles de l'industrie métallurgique.

Les divers éléments sont classés par ordre alphabétique, soit: Al, Sb, As, Be, Pb, B, Cd, Cr, métaux précieux, Ga, Ge, In, Co, C, Cu, Li, Mg, Mn, Mo, Ni, P, Hg, Se, Si, Ta–Nb, Te, Th, Ti, U, V, Bi, W, Zn, Sn, et Zr. Cet ouvrage ne fait mention d'aucune considération théorique, il est essentiellement pratique. Chaque élément est traité séparément. Leur dosage, ainsi que celui des impuretés les plus importantes qui les accompagnent, sont décrits pour les milieux suivants: produits bruts (minerais), produits intermédiaires de la fabrication, métal pur, divers alliages et les produits secondaires indispensables aux différents stades de la purification.

Toutes les méthodes sont éprouvées et décrites avec minutie, qualité indispensable lorsqu'on veut "standardiser" les diverses opérations analytiques. Plus de 50 chimistes, travaillant dans ce domaine, ont confronté les méthodes et ont participé à l'élaboration de cet ouvrage. Certaines méthodes sont basées sur des opérations classiques telles que la gravimétrie et la volumétrie, d'autres sont empruntées aux méthodes physico-chimiques d'analyses telles que la spectrophotométrie, la fluorimétrie, la potentiométrie, la polarographie et l'électro-gravimétrie. Pour chacune des méthodes les auteurs indiquent le mode de séparation, le principe du dosage, la précision, le domaine d'utilisation, l'appareillage nécessaire et la marche à suivre (avec liste des réactifs et leur préparation).

Si cet ouvrage, clair et bien présenté, s'adresse plus spécialement aux chimistes métallurgistes, il peut néanmoins rendre de grands services à tout chimiste, aussi bien chercheur qu'industriel, s'intéressant aux dosages des métaux non ferreux et des principales traces d'impuretés qui les accompagnent.

W. HAERDI (Genève)

C. L. Lewis, W. L. Ott and N. M. Sine, *The Analysis of Nickel*, International Series of Monographs on Analytical Chemistry, Vol. 28, Pergamon Press Limited, Oxford, 1966, x + 215 pp., price 55 s.

The composition of certain metals and alloys intended for nuclear engineering purposes must meet stringent requirements. In recent years it has become necessary to determine some elements that were not previously determined in these materials, and, in many instances, current analytical procedures have been totally lacking in sensitivity. It is clearly with this background that *The Analysis of Nickel* has been published by authors who have worked in this field for many years, and a record of their wide experiences is now available to analysts with similar interests. The book also draws on other sources of related information, and is supported by adequate lists of references.

Chapters in the book include Sampling, Optical-spectrochemical, X-Ray spectrochemical, Spectrophotometric and Polarographic Methods, and the Determination of Carbon, Sulphur, and Gases, together with Other Methods of Analysis (flame and atomic-absorption spectrophotometry, and spark-source solids mass spectrometry).

The determination of nitrogen in metallurgical materials by the vacuum-fusion procedure is always a source of controversy, and this subject does not receive the detailed comment in this book that it merits. The Kjeldahl method for determining nitrogen is invariably accepted as being reliable, but no details of this method appear in the book. Whilst the procedure is straightforward, it would have been interesting to ascertain the extent to which the indophenol reaction is used by the authors, especially since the use of this more reliable method of completing the nitrogen determination might have resolved some of the discrepant nitrogen values reported on pp. 176 and 177.

Overall, however, the book is well worth purchasing by anyone with a specialised interest in the analysis of nickel.

W. T. Elwell (Birmingham)

Anal. Chim. Acta, 39 (1967) 278

Encyclopedia of Industrial Chemical Analysis. Vol. I. General Techniques A–E, Edited by F. D. Snell and C. L. Hinton, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1966, xv + 763 pp., price 340 s (260 s for subscribers to the complete set).

This is the first volume of a new encyclopaedia in which the "present state of the art" of industrial analytical chemistry is to be delineated. The first Part deals with General Techniques, of which Volume I covers A–E: Azeotropy rubs shoulders with Balances, and Chromatographic methods with Color designation and specification. There are to be 2 further volumes to cover the alphabet and the main body of the encyclopaedia, which will deal with the analysis of specific materials, will start at Volume IV, and run to an unspecified number of volumes.

The wisdom of starting yet another new series of volumes on analytical chemistry must be questioned, amidst the numerous treatises, handbooks, monograph series, etc. which are pouring from the presses and remain largely undigested, on account of their sheer bulk, by those who could most profit from them. The treatment in this first volume leads one to suppose that the degree of "pottedness" in the chemistry will be intermediate between the handbooks and the treatises of analytical chemistry. A proper estimate of the work will be impossible until the volumes of Part II appear, but it does seem that the editors will have to be extremely careful if a plain rehash of existing literature is to be avoided.

As is proper for industrial analysis, practice is emphasized rather than theory, and the discussions of methods are well illustrated by examples of actual procedures as well as by tables, diagrams and photographs. The section on Coulometry and Coulometric titrations may serve as a random example of the style of treatment: the general introduction (3 pp.) is followed by sections on theory (4 pp.), equipment ($5\frac{1}{2}$ pp.) and typical applications (4 pp.) and a bibliography (1 p.). But there is no indication of the large number of reagents that can be generated electrolytically, so that one is left with a rather restricted view of the general method. Strangely, air pollution has been regarded as a general technique instead of air as a material to be analysed, and this volume contains detailed procedures for all the main contaminants.

Finally one wonders who will buy these volumes. Even libraries may blench at the prospect of *ca.* £13 a volume for the full set. For industrial analysts, individual purchase must be largely impossible and indeed unprofitable, considering that few will be interested in more than particular portions of the whole text.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 39 (1967) 278–279

W. T. ELWELL AND J. A. F. GIDLEY, *Atomic-Absorption Spectrophotometry*, 2nd (revised) Edn., International Series of Monographs on Analytical Chemistry, Vol. 6, Pergamon Press, Oxford, 1966, xii + 138 pp., price 42 s.

While retaining some material from the first edition, this second edition has been expanded to almost twice the length and so extensively revised and rewritten that it is essentially a new and very much more comprehensive and valuable textbook. With the analyst very much in mind, the authors give a good account of theory, equipment, practice and future development, written in a style with high information content yet lucid and pleasing. An excellent chapter, *Comparison with other analytical procedures*, puts atomic absorption into perspective, not as a panacea for all the analyst's ills but as yet another rapid, simple and relatively inexpensive addition to his armoury.

The remainder of the book deals with analytical applications, element by element, with references to work up to and including 1966. A useful pull-out sheet tabulates, in some detail, the characteristics of commercial instruments available to date.

This is a book no analytical laboratory can afford to be without.

A. M. URE (Aberdeen)

Anal. Chim. Acta, 39 (1967) 279

G. GOTTSCHALK, *Einführung in die Grundlagen der chemischen Materialprüfung*, S. Hirzel Verlag, Stuttgart, 1966, xv+188 S., Kart. DM 21.60.

Mit seinem zweiten Werk über die Anwendung statistischer Methoden in der analytischen Chemie leistet der Autor einen sehr wertvollen Beitrag auf einem Gebiet, für das trotz zunehmender Bedeutung ein sehr fühlbarer Mangel an diesbezüglicher deutschen Büchern herrscht. Auch Leser mit spärlichen Kenntnissen statistischer Methoden und ihren richtigen Anwendungen werden in dem vorliegenden ersten Band der Reihe *Analytische Chemie in Theorie und Praxis* (Herausgeber E. BLASIUS UND G. GOTTSCHALK) eine ausgezeichnet ausgewählte Reihe von 38 Problemen aus verschiedensten Bereichen der analytischen Chemie mit den zugehörigen mathematisch–statistischen Verfahren von steigendem Schwierigkeitsgrad kombiniert finden, mit deren Hilfe es leicht ist, sich sowohl allgemein über das Thema zu informieren, als auch ein gegebenes Problem der angemessenen Behandlung zu unterziehen. Das Buch kann jedem, der mit der Behandlung und Auswertung analytischer Aufgaben befasst ist, bestens empfohlen werden.

H. MALISSA (Wien)

Anal. Chim. Acta, 39 (1967) 280

W. E. HARRIS AND H. W. HABGOOD, *Programmed Temperature Gas Chromatography*, J. Wiley and Sons, Inc., New York, 1966, xvi+305 pp., price 83 s.

The gradual increasing of the temperature of a gas chromatography column as the components of a mixture are passing through it has the effect of accelerating the passage of the longer retained components. This makes possible more rapid and efficient resolution than is usual by the more traditional or isothermal technique, of a mixture of substances whose boiling points vary over a wide temperature range. The technique, known as programmed temperature gas chromatography, is becoming increasingly popular.

This book outlines the principles of gas chromatography, and shows how these may be used with advantage in the programmed temperature technique. It discusses the principles in simple mathematical terms, and illustrates their application to experiments. Whilst the book deals fairly with experimental devices, it emphasises the principles, and in this respect sets a good standard for works on gas chromatography. It includes some useful rules for the presentation of results obtained using the technique.

Gas chromatography is an easily applied and very effective analytical technique, yet the complete exploitation of its potentialities requires careful attention to fundamental principles. It is for users of the technique to decide how great an effort they can afford to devote to improving the conditions for applying gas chromatography to their own problems. The solution of the immediate problem must take priority over the perfection of the technique, but in the author's experience too few users of gas chromatography understand sufficiently its principles.

All who consider the use of the programmed variation in column temperature in gas chromatography should read this book, even if many ignore some of the details of the arguments. Those who wish to study programmed temperature gas chromatography thoroughly will find the book indispensable.

C. R. PATRICK (Birmingham)

Anal. Chim. Acta, 39 (1967) 280

G. KRAFT, *Handbuch der analytischen Chemie,* Herausgegeben von W. FRESENIUS UND G. JANDER, *3. Teil. Quantitative Bestimmungs- und Trennungsmethoden. Band IV αβδ. Elemente der vierten Hauptgruppe II–IV. Germanium. Blei,* Springer-Verlag, Berlin, 1966, xvi+222 S., ganzleinen DM 64.—. Steif geheftet DM 59.—.

Comme tous les fascicules de cet ouvrage, celui-ci est un modèle, tant par l'abondance de renseignements qu'il donne que par le soin et la précision avec lesquels les méthodes sont décrites.

La partie concernant le plomb comprend un chapitre sur la mise en solution, un autre sur les méthodes gravimétriques, y compris l'électrogravimétrie. Viennent ensuite les méthodes titrimétriques, aussi bien volumétrique que potentiométrique, ampérométrique, coulométrique qu'enthalpique, puis la spectrophotométrie.

Enfin quelques pages sont consacrées aux déterminations polarographiques, optiques et radiochimiques. On peut regretter qu'une place aussi réduite ait été réservée aux méthodes physiques et physico-chimiques.

Il n'en reste pas moins que cet excellent ouvrage doit être vivement recommandé, mais est-il nécessaire de le faire car il est depuis longtemps universellement connu de tous les chimistes analystes.

D. MONNIER (Genève)

F. E. BEAMISH, *The Analytical Chemistry of the Noble Metals,* International Series of Monographs in Analytical Chemistry, Vol. 24, Pergamon Press, Oxford, xiv+608 pp., price 120 s.

Anyone reading this book is bound to conclude that it is an authoritative source of reliable information written by an undisputed expert in this area of analytical chemistry. It provides a virtually complete coverage of classical and modern methods for the separation and determination of osmium, ruthenium, iridium, rhodium, palladium, platinum and gold.

The first chapter is devoted to the important subject of sample preparation, and includes detailed information on the action of acids and bases on the noble metals, their behaviour in chlorine atmospheres, and the effect of oxygen or air at elevated temperatures.

A comprehensive account of separation procedures is given in Chapter 2, which includes detailed sections on precipitation, solvent-extraction, ion-exchange and chromatographic methods. Fire-assay methods for the analysis of ores are critically discussed, and methods for the assay of gold cyanide solutions are described.

Separate chapters are devoted to gravimetric, volumetric, spectrophotometric and spectrochemical methods for determining the 7 metals.

This work is not merely a collection of published papers; it is well supported throughout by the author's own experience, and various potential areas of useful research are suggested. It is highly recommended, and will doubtless be regarded as the standard work on the subject for many years to come.

D. F. WOOD (Birmingham)

The Determination of Toxic Substances in Air: A Manual of ICI Practice, Edited by N. W. Hanson, D. A. Reilly and H. E. Stagg, 2nd Edn., 1965, Heffer, Cambridge, xii+200 pp., price 50 s.

This is a rather complete revision of a volume first published in 1956, with tests for some 10 additional materials, together with notes on the use of gas chromatography in some analyses. The second phrase in the title is precise. This is no philosophical treatise nor textbook, but a field manual having as its sole purpose the listing of methods in use by ICI for determining toxicants at concentrations near their official Threshold Limit Values in and around chemical works. The writing is very clear. The point requires emphasis that, as a manual permitting duplication of techniques in use by a large chemical manufacturer, this book is difficult to fault.

However, as a generalized manual for measuring toxic materials in the air (which is certainly implied both in the title and in the foreword), the book is frighteningly poor. The bulk of the techniques are very unselective, and interferences are discussed briefly if at all; means of averting interference are not mentioned. The sensitivities are in many cases so marginal that the reduction of a Threshold Limit Value will at best leave the analyst with no records of occurrences near the new value, and at worst may leave him with no method.

The bibliography is rudimentary, but what there is suggests very little knowledge of non-British work. The chapter on "The Preparation of Atmospheres of Known Composition" ignores extensive reviews as well as original papers in the literature. Such well-known analytical methods as those of West and Gaeke for sulfur dioxide; of Saltzman and of Jacobs and Hochheiser for nitrogen oxides; the determination of formaldehyde by chromotropic acid; all of these are omitted. Ozone, a truly toxic material, is not discussed, nor is acrolein; presumably these do not occur in ICI plants. The magnificently sensitive and selective technique of atomic absorption spectrometry is likewise not mentioned.

Aside from a few applications of gas chromatography, there is little in the book which could not have been written 20 years ago. It may be that airborne toxicants are so segregated (and concentrated) in ICI plants that the crudest methods suffice for their measurement; if these conditions are not met, many of the methods described will fail. The techniques described in this volume should be regarded with great skepticism in other environments. For determinations out-of-doors they are nearly totally inappropriate.

J. P. Lodge, Jr. (Boulder)

Anal. Chim. Acta, 39 (1967) 282

K. B. Wiberg, *Computer Programming for Chemists*, Frontiers in Chemistry Series, Edited by R. Breslow and M. Karplus, W. A. Benjamin, Inc., New York, 1965, viii+269 pp., price $12.50 (in U.S.A.; $13.75 elsewhere).

Computing is playing an increasingly important part in both the pure and applied sciences; many branches of chemistry involve lengthy calculations that lend themselves to treatment by computer. A book that explains the ways of computing in Fortran and gives worked examples would be a useful addition to any chemist's bookshelf. The text under review has been written with this need in mind. However, it has a most irritating feature. Reading the volume, one is struck by a feeling of *déjà vu* as one turns from pages 75–78 to pages 82–85 and finds Fortran II and Fortran IV described in identical sentences and identical examples. For good measure the section on the use of FAP (Fortran Assembly Program) (p. 107–131) is repeated word for word in the section dealing with MAP (Macro Assembly Program) (p. 131–154). Professor WIBERG has also been less than lucky with the typography. Explaining the difference between the use of numbers and index letters, he unfortunately chose the figure one and a lower case L as his examples, both of which appear in the book as identically printed "l"-s, leaving the reader guessing.

However, he describes some very useful programs dealing with a variety of subjects. For each one he gives a complete listing, a general description of the way the data have to be arranged, and a specific example with input data and resulting output. The programs range from simple ones, like the calculation of the slope and intercept of a line by the method of least squares, to sophisticated ones dealing, for example, with NMR spectra and the calculation of the energies of aromatic systems by POPLE's method. Some of these include subroutines to instruct the computer to plot the results.

L. M. GILBERT (Birmingham)

Anal. Chim. Acta, 39 (1967) 282–283

PUBLICATIONS RECEIVED

V. I. GOL'DANSKII, *The Mössbauer Effect and its Applications in Chemistry*, D. Van Nostrand Company, Inc., Princeton, N.J., 1966, 119 pp., price 40 s. ($4.95) (paperback).

N. S. POLUEKTOV, *Techniques in Flame Photometric Analysis*, D. Van Nostrand Company, Inc., Princeton, N.J., 1966, xvi+219 pp., price 40 s. ($4.95) (paperback).

Wet Combustion and Catalytic Methods in Microanalysis, Edited by J. A. KUCK, Methods in Microanalysis Series, Vol. 2, Gordon and Breach Science Publishers, New York, 1966, xx+412 pp., price $21.
This volume contains some of the microchemical research papers of A. P. TERENT'EV and J. KÖRBL up to 1964.

T. C. BRUICE AND S. J. BENKOVIC, *Bioorganic Mechanisms*, Vol. II, W. A. Benjamin, Inc., New York, 1966, viii+419 pp., price $25.00.

Biochemical Preparations, Vol. 11, Edited by A. C. MAEHLY, J. Wiley and Sons, Inc., New York, 1966, viii+147 pp., price 60 s.

P. FEILLET, *Contribution à l'Etude des Protéines du Blé. Influence des Facteurs Génétiques, Agronomiques et Technologiques*, Institut National de la Recherche Agronomique, Versailles, 1966, 94 pp., prix 16 NF.

Anal. Chim. Acta, 39 (1967) 283–284

Progress in Nuclear Energy. Series IX. Analytical Chemistry, Vol. VII, Edited by H. A. ELION AND D. C. STEWART, Pergamon Press, Ltd., Oxford, 1966, v+288 pp., price 90 s.

This book contains the following reviews and tables: Electron Diffraction Techniques and their Applications to the Study of Surface Structure (R. K. HART); Liquid Scintillator Solutions in Nuclear Physics and Nuclear Chemistry (D. L. HORROCKS); In-line Analytical Instrumentation of Nuclear Fuel Reprocessing Plants (C. R. MCGOWAN AND J. K. FOREMAN); The Ion Microprobe Mass Spectrometer (A. E. BARRINGTON, R. F. K. HERZOG AND W. P. POSCHENRIEDER); A Table of Coefficients for the Microprobe Analyst (R. D. DEWEY); Tables of X-Ray Data (R. D. DEWEY, R. S. MAPES AND T. W. REYNOLDS).

G. B. KAUFFMAN, *Alfred Werner: Founder of Coordination Chemistry*, Springer-Verlag, Berlin, 1966, xvi + 127 pp., paperback DM 24.—.

This book is a definitive biography of Alfred Werner (1866–1919) and includes a complete bibliography of his published work.

G. W. EWING, *Analytical Instrumentation: A Laboratory Guide for Chemical Analysis*, Plenum Press, New York, 1966, xix+151 pp., price $7.50.

Chapter headings: The Electrical Modules; Electroanalytical Modular Instruments; Optical Instruments; Analytical Experiments; Experiments in Instrument Evaluation.

This manual is designed to accompany the modular system of analytical instruments (A.R.F. Products, Inc.) for teaching purposes.

Chromatographie et Méthodes de Séparation Immédiate, Tome I, II, sous la direction de G. PARISSAKIS, Union of Greek Chemists, Athens, 1966. Tome I, 426 pp.; Tome II, 317 pp., price (2 vols. including postage) $ 11.00.

These volumes contain the Proceedings of a Symposium held in Athens in September, 1965, organized by the "Groupement pour l'Avancement des Méthodes Spectrographiques, France" and the Union of Greek Chemists.

F. J. WELCHER, *Chemical Solutions. Reagents useful to the Chemist, Biologist and Bacteriologist*, D. van Nostrand Company, Inc., Princeton, 1966, vii+404 pp., price 40 s.

This is a paperback reprint of the original 1942 edition.

The Chemical Formulary, Vol. XIII, Editor-in-Chief H. BENNETT, Chemical Publishing Company, Inc., New York, 1967, 447 pp., price $ 8.00.

This book contains recipes for the preparation of adhesives, cement and related products, cosmetics and drugs, emulsions, foods and beverages, inks, metals and metal cleaners, paints and lacquers, paper, polish, pyrotechnics, rubber, plastics, waxes, soaps, cleaners, textile specialities and other products. Lists of chemicals and suppliers are appended.

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